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# (12) UK Patent Application (19) GB (11) 2 307 238 (13) A

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293/00  
CAS ONLINE, WPIL

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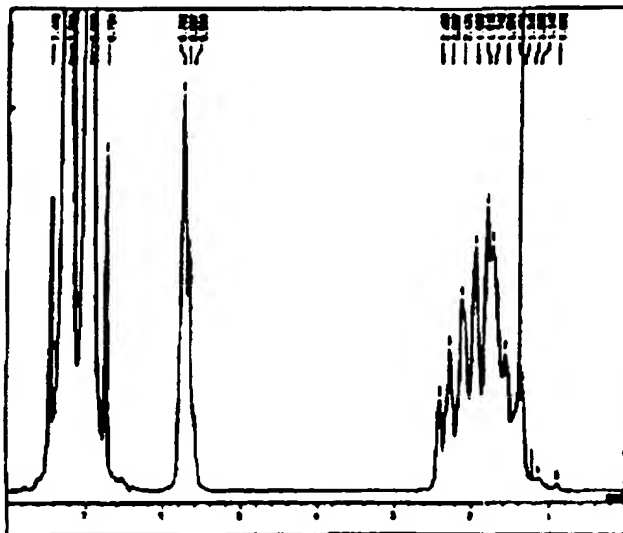
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(54) Improved cyclic conjugated diene polymer and process for producing the same

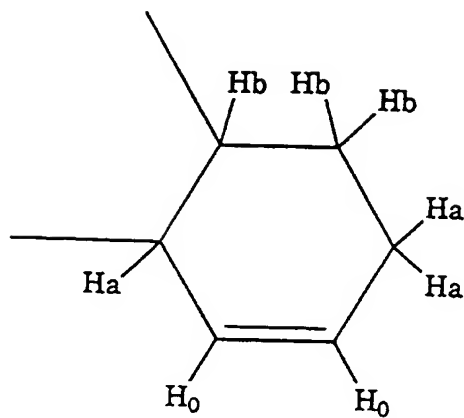
(57) A cycle conjugated diene polymer wherein the main chain comprises the units of at least one cycle conjugated diene monomer alone or a mixture thereof with the units of at least one other monomer copolymerizable with the diene monomer, wherein the diene monomer units are linked to each other in the main chain through 1,2 and 1,4-bonds in a comparatively high molar ratio of the 1,2-bond to the 1,4-bond, and which has a comparatively narrow molecular weight distribution and improved thermal and mechanical characteristics. The invention also discloses an industrially advantageous process for producing the diene polymer having such excellent features by using a specific catalyst.



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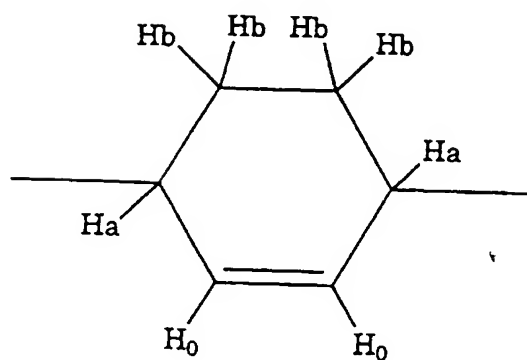
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**FIG. 1 (a)**



**1,2 - Bond**

**FIG. 1 (b)**

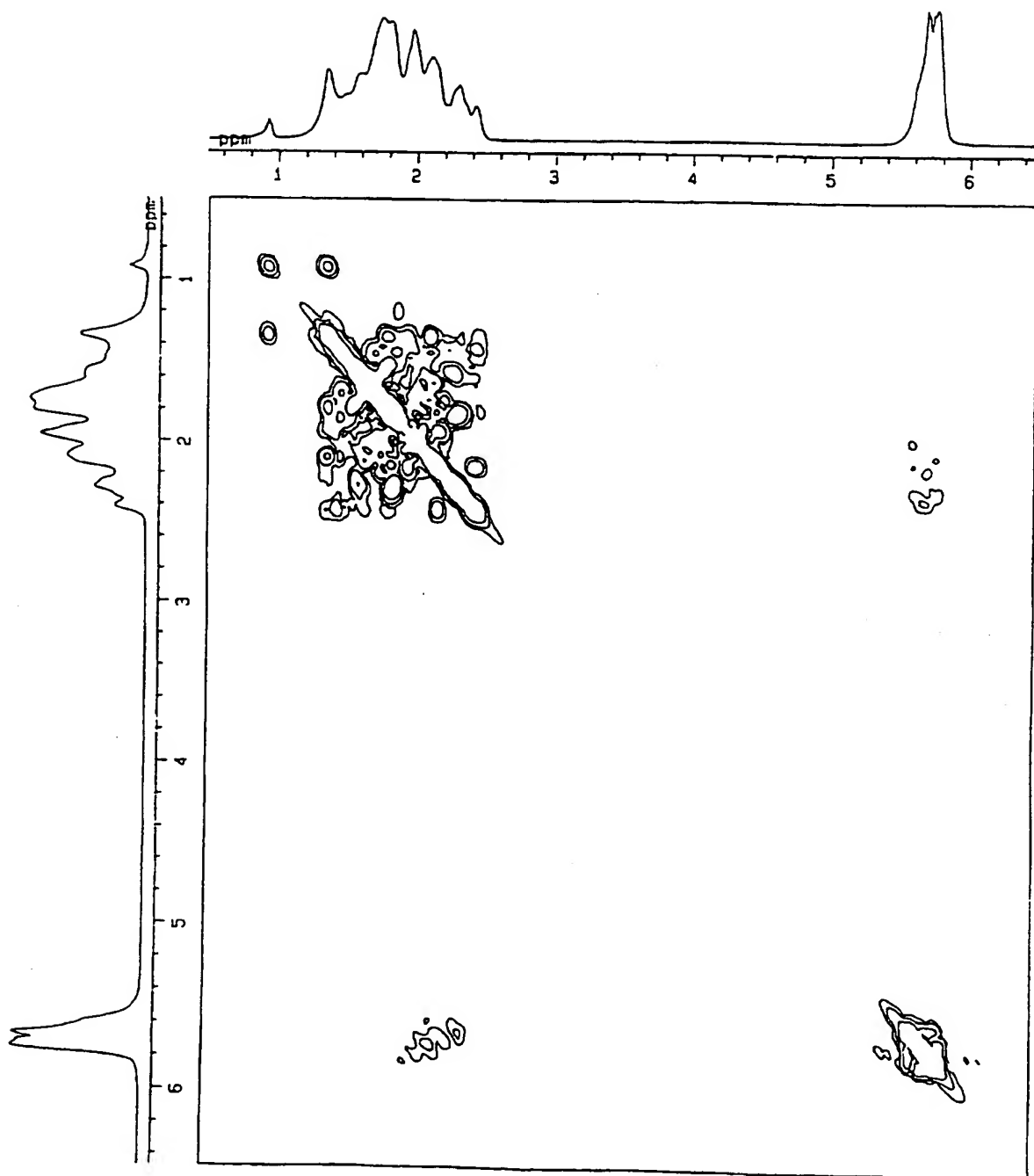


**1,4 - Bond**



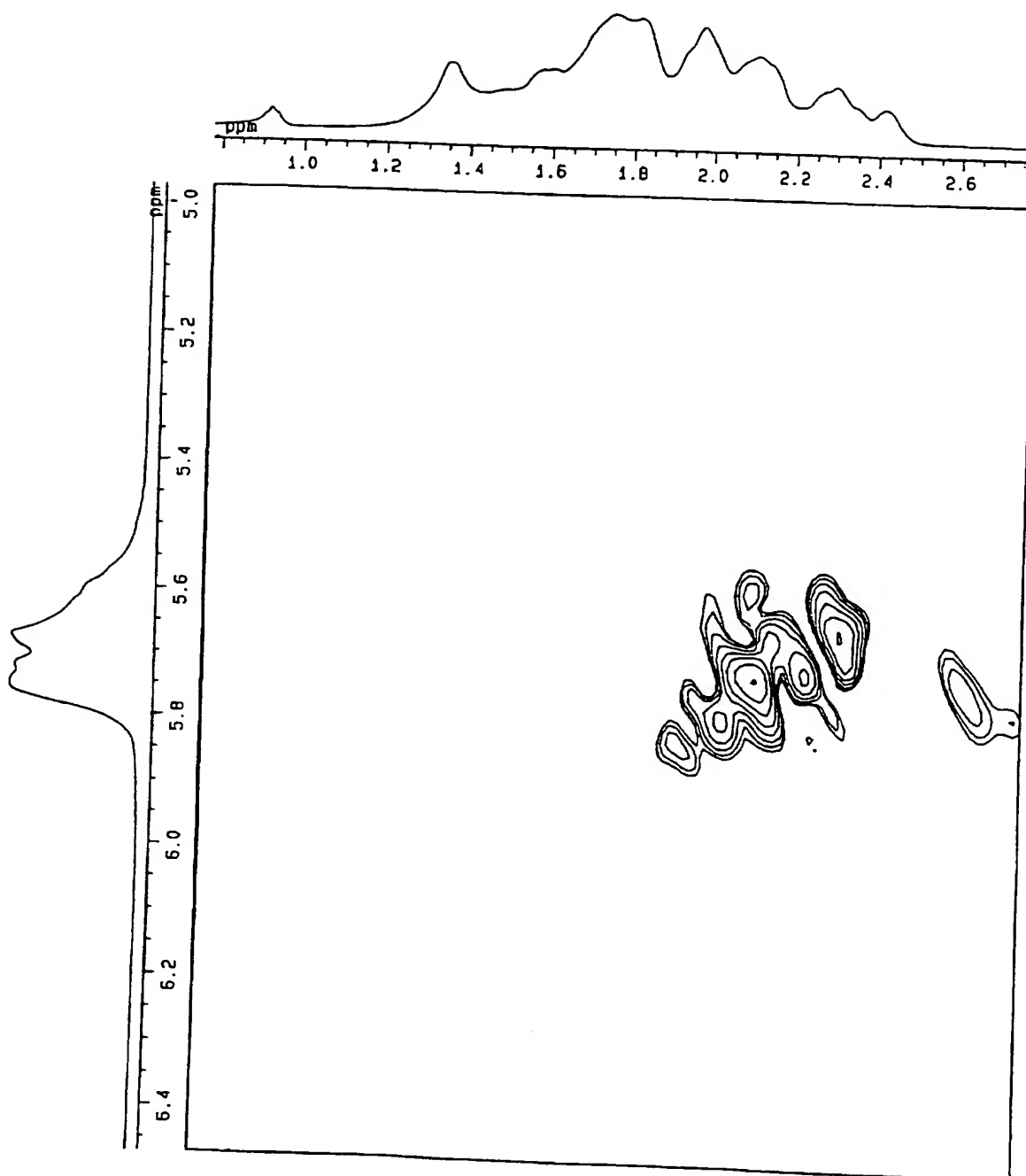
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FIG. 2



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FIG. 3



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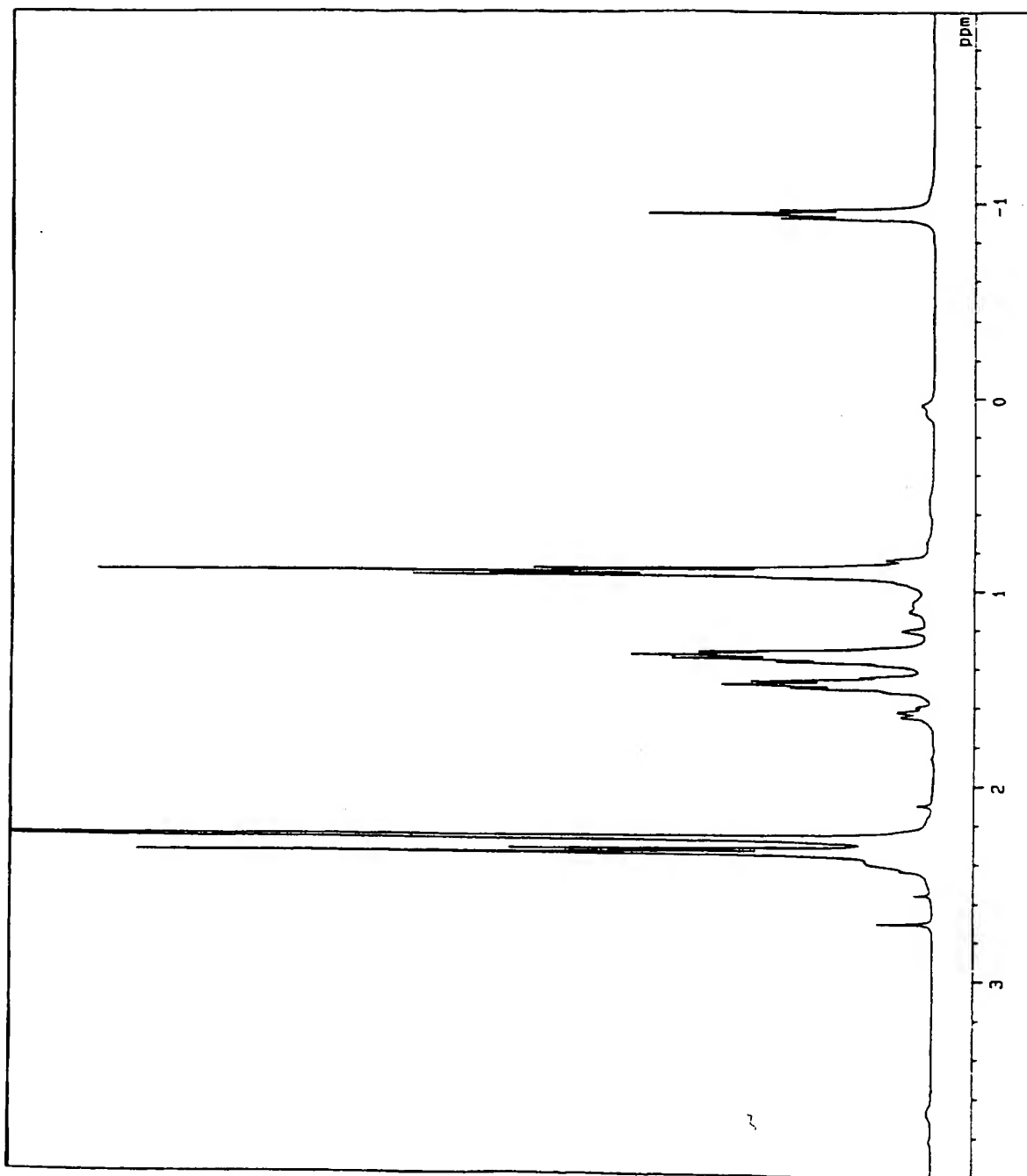


FIG. 4

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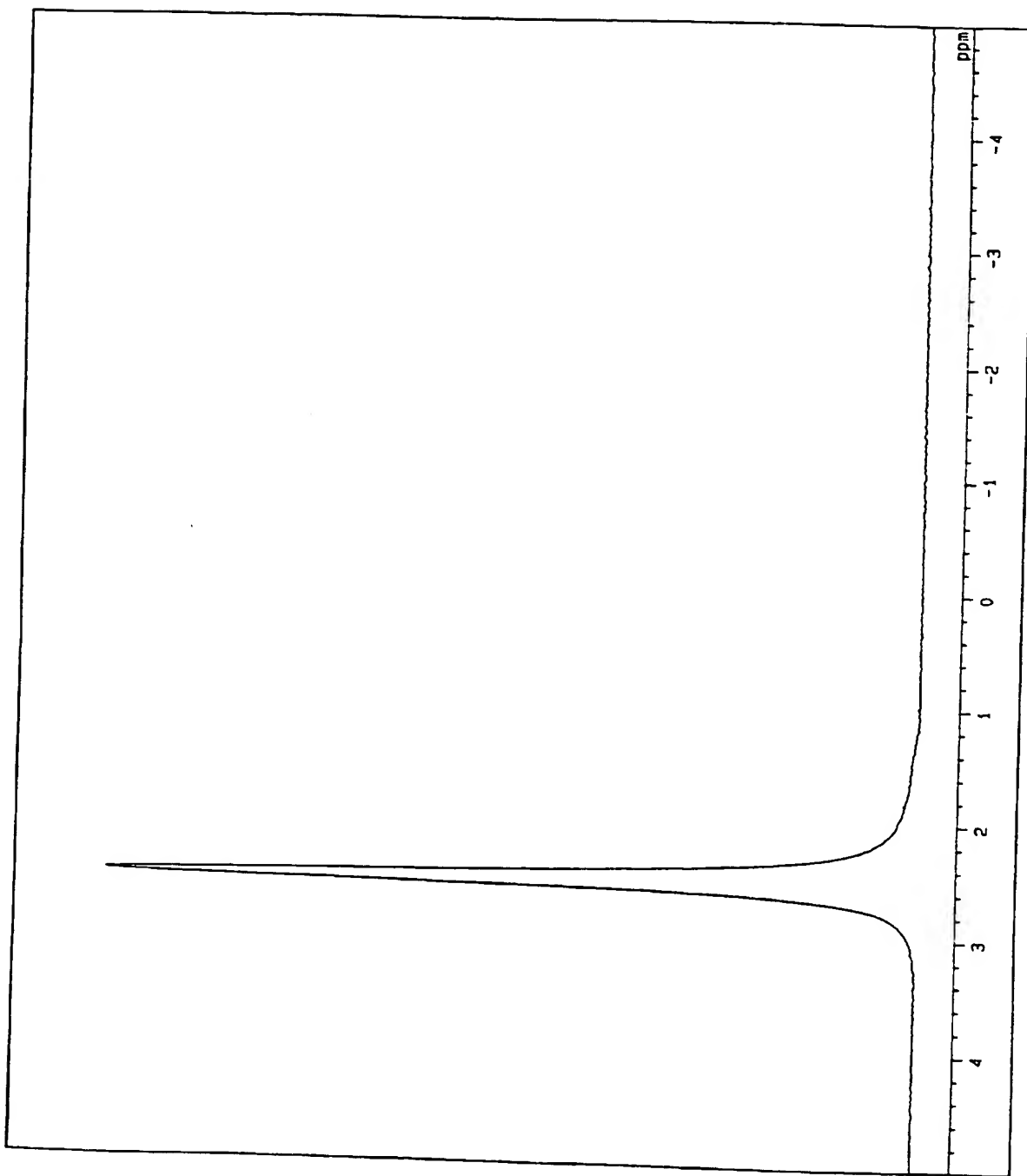


FIG. 5

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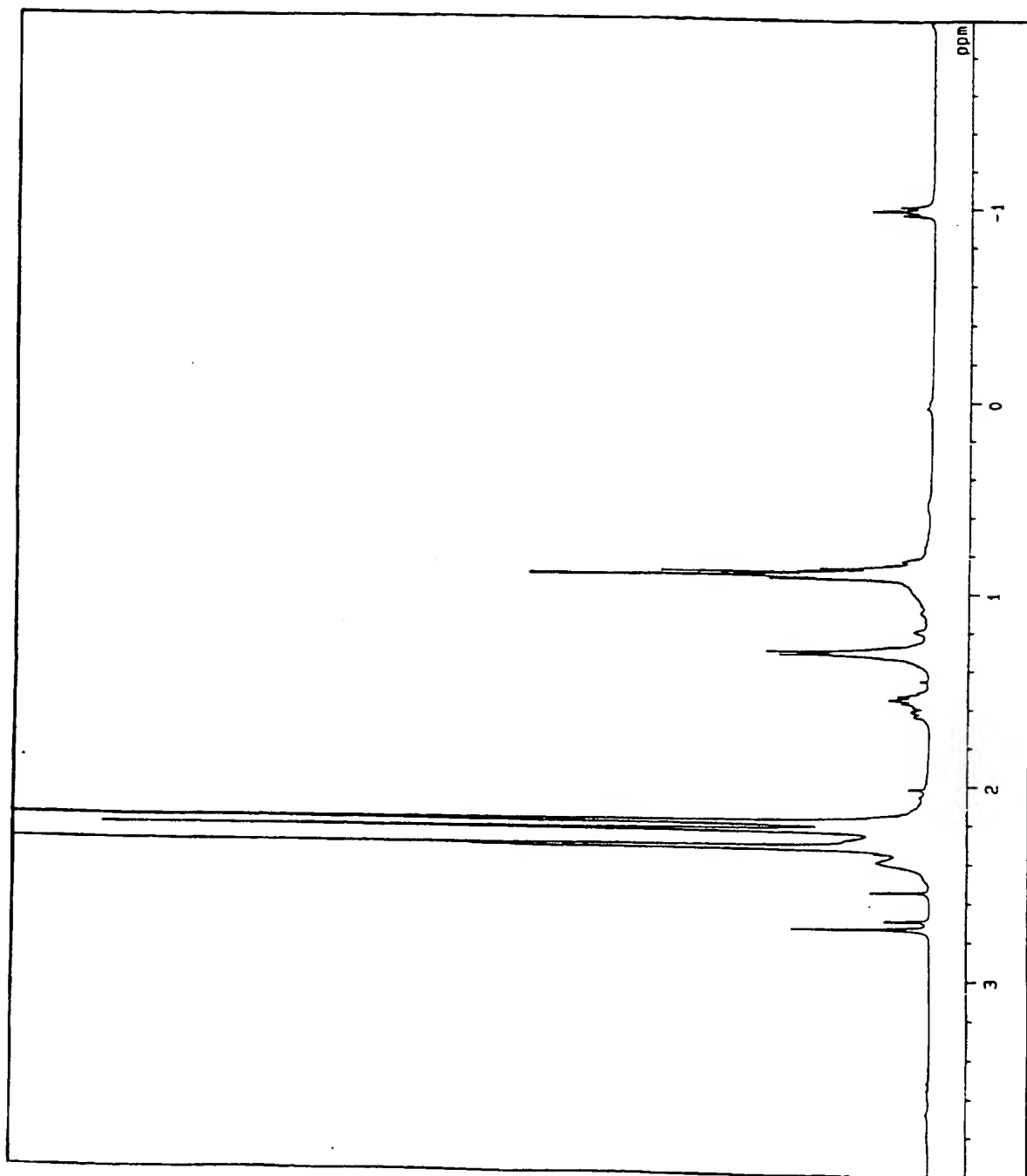


FIG. 6

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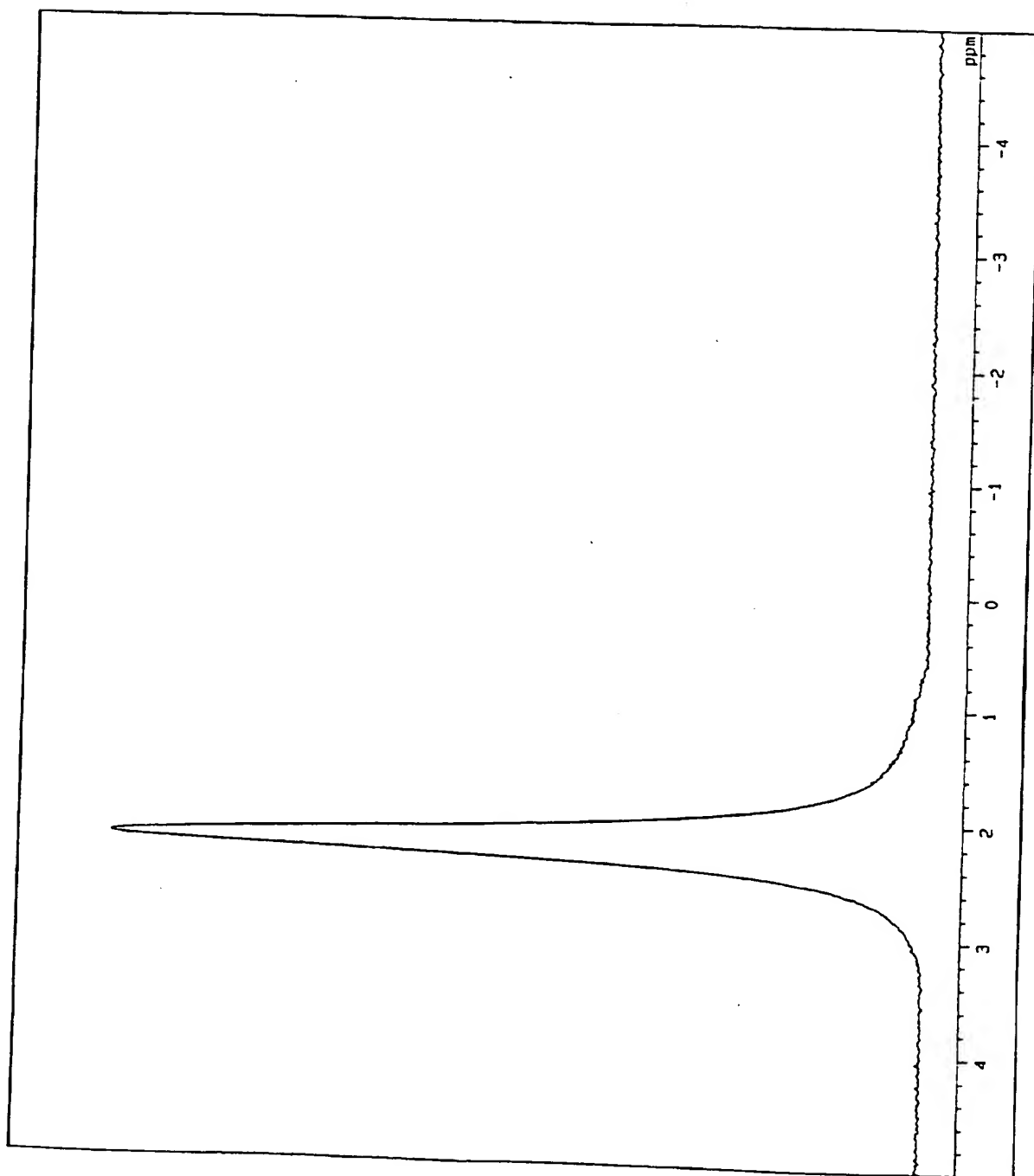


FIG. 7

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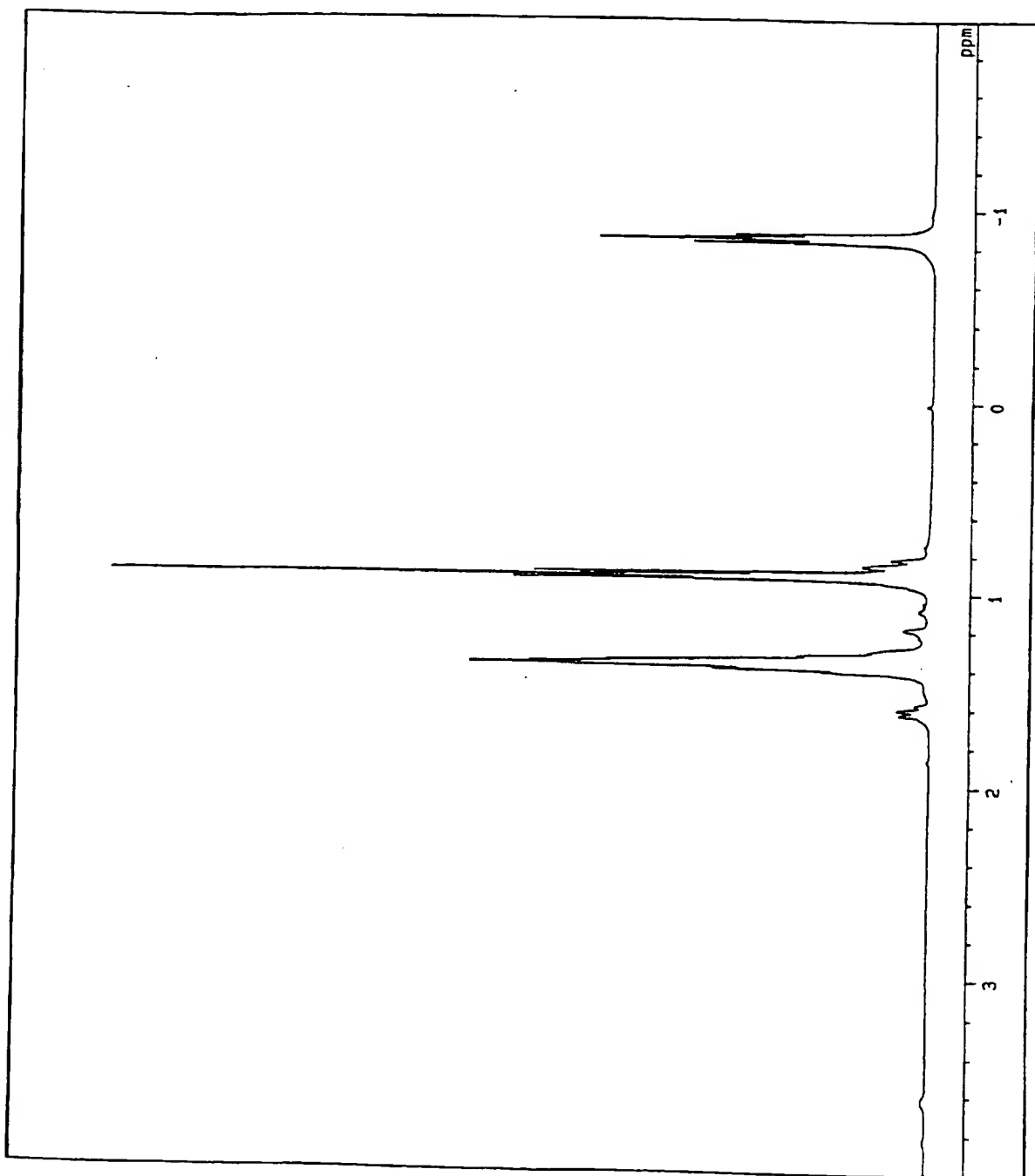


FIG. 8

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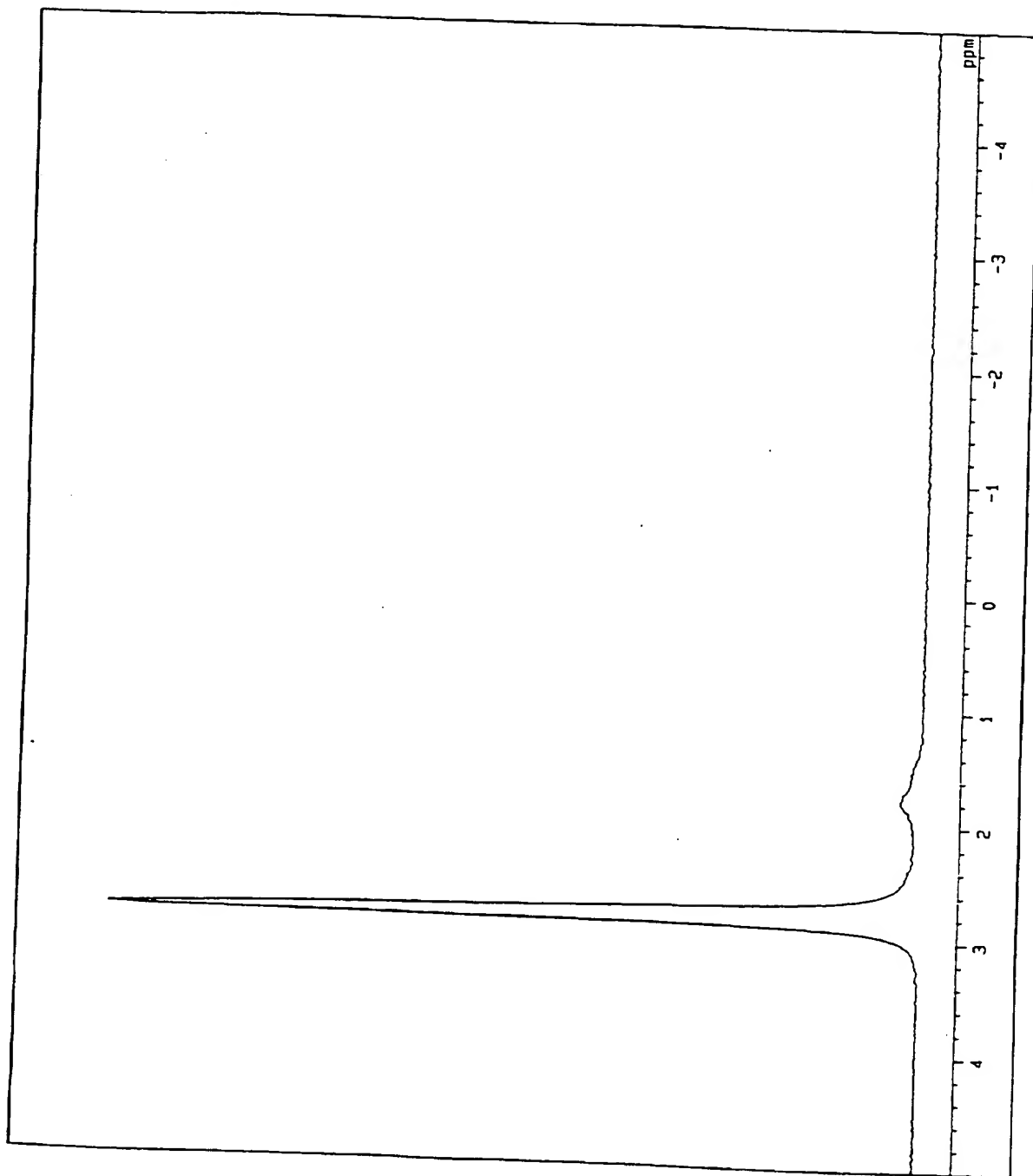


FIG. 9



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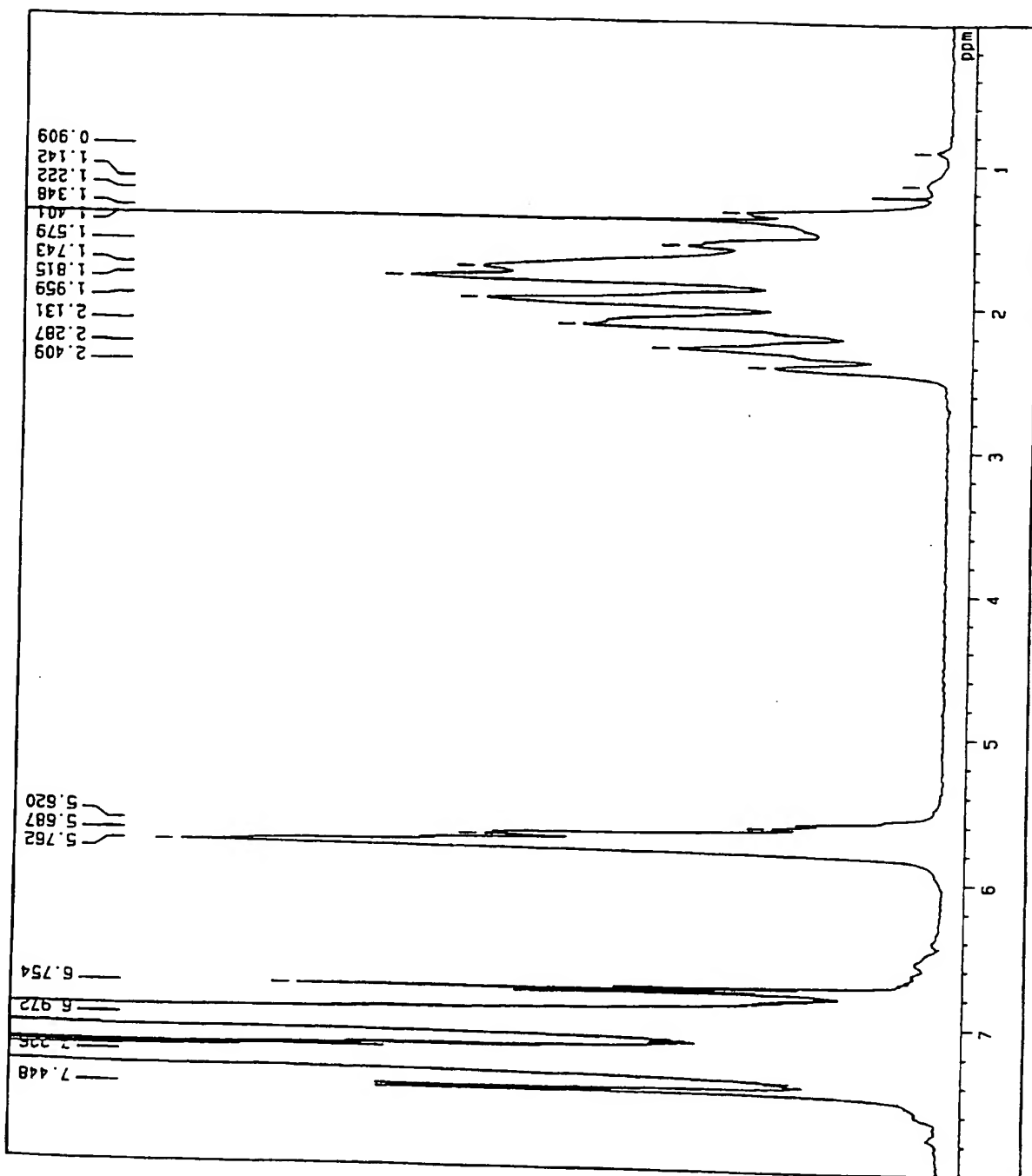


FIG. 10

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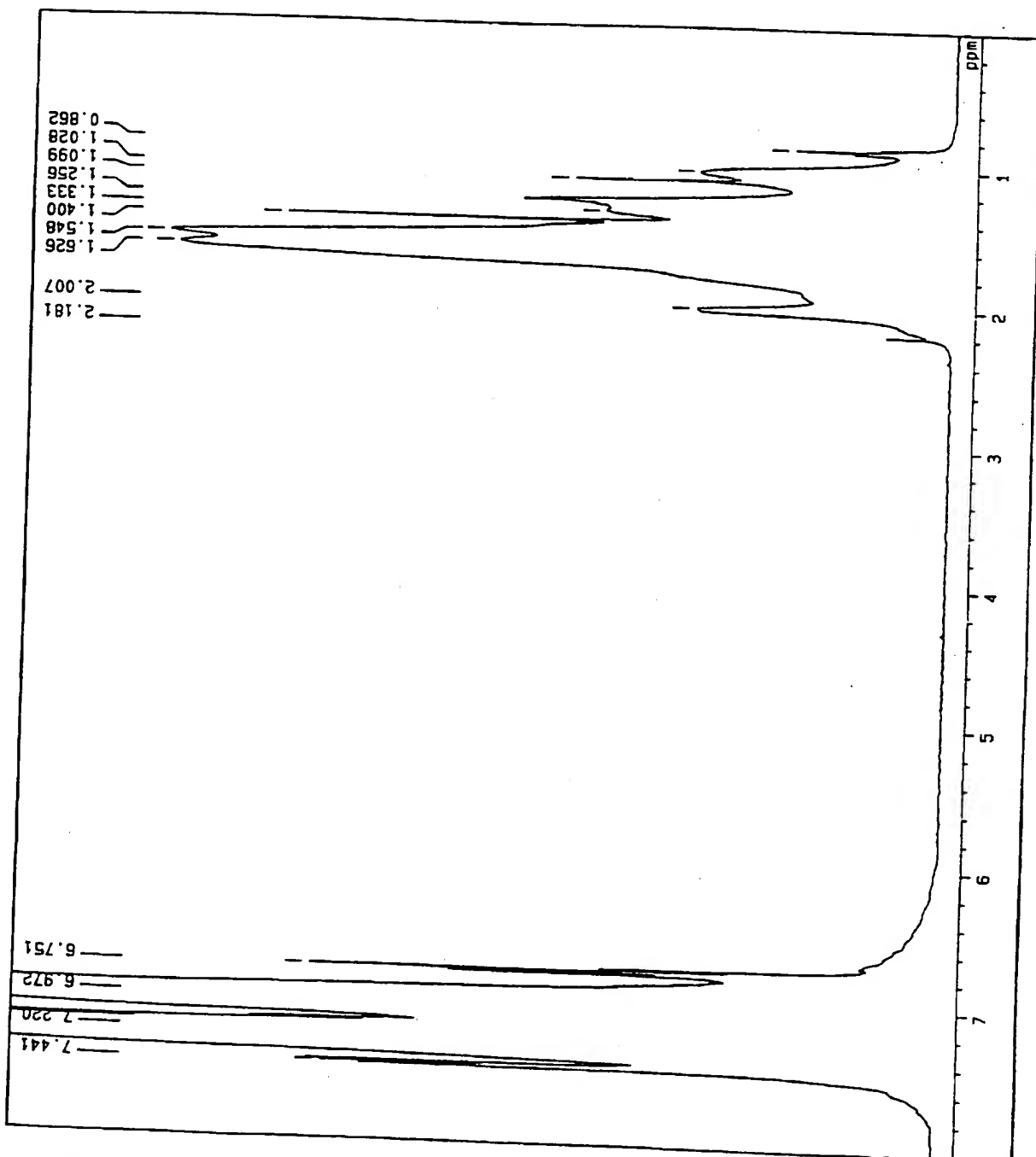


FIG. 11

1H NMR spectrum of compound 10a in CDCl<sub>3</sub>. The x-axis is chemical shift in ppm, ranging from 0 to 10. The spectrum shows several peaks:

- 0.813
- 1.107
- 1.400
- 1.462
- 1.687
- 1.814
- 1.977
- 2.102
- 2.136
- 2.296
- 2.410
- 4.788
- 4.976
- 5.204
- 5.673
- 5.760
- 6.772
- 6.972
- 7.296
- 7.431

**FIG. 12**

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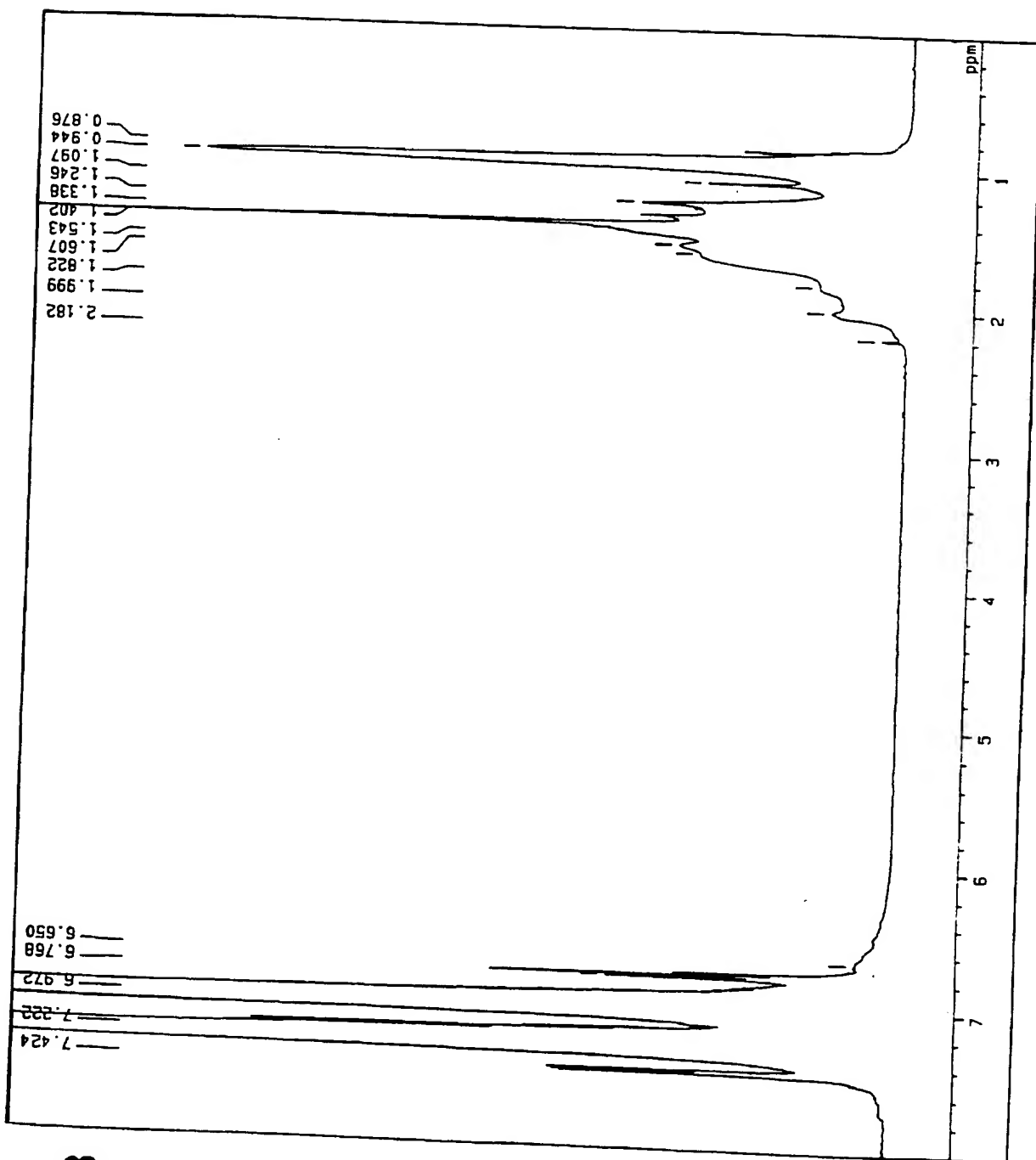


FIG. 13

**FIG. 14**

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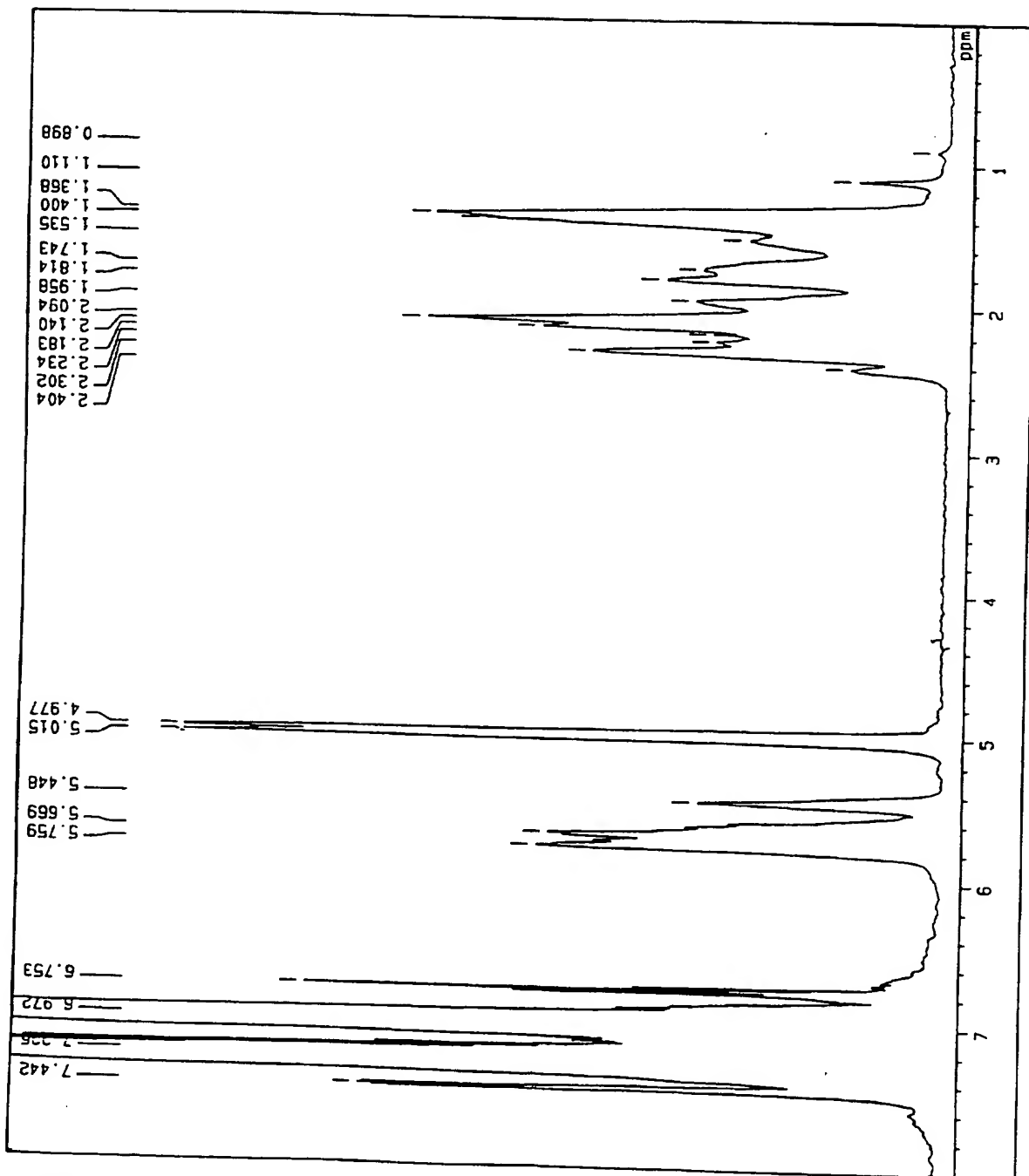


FIG. 15

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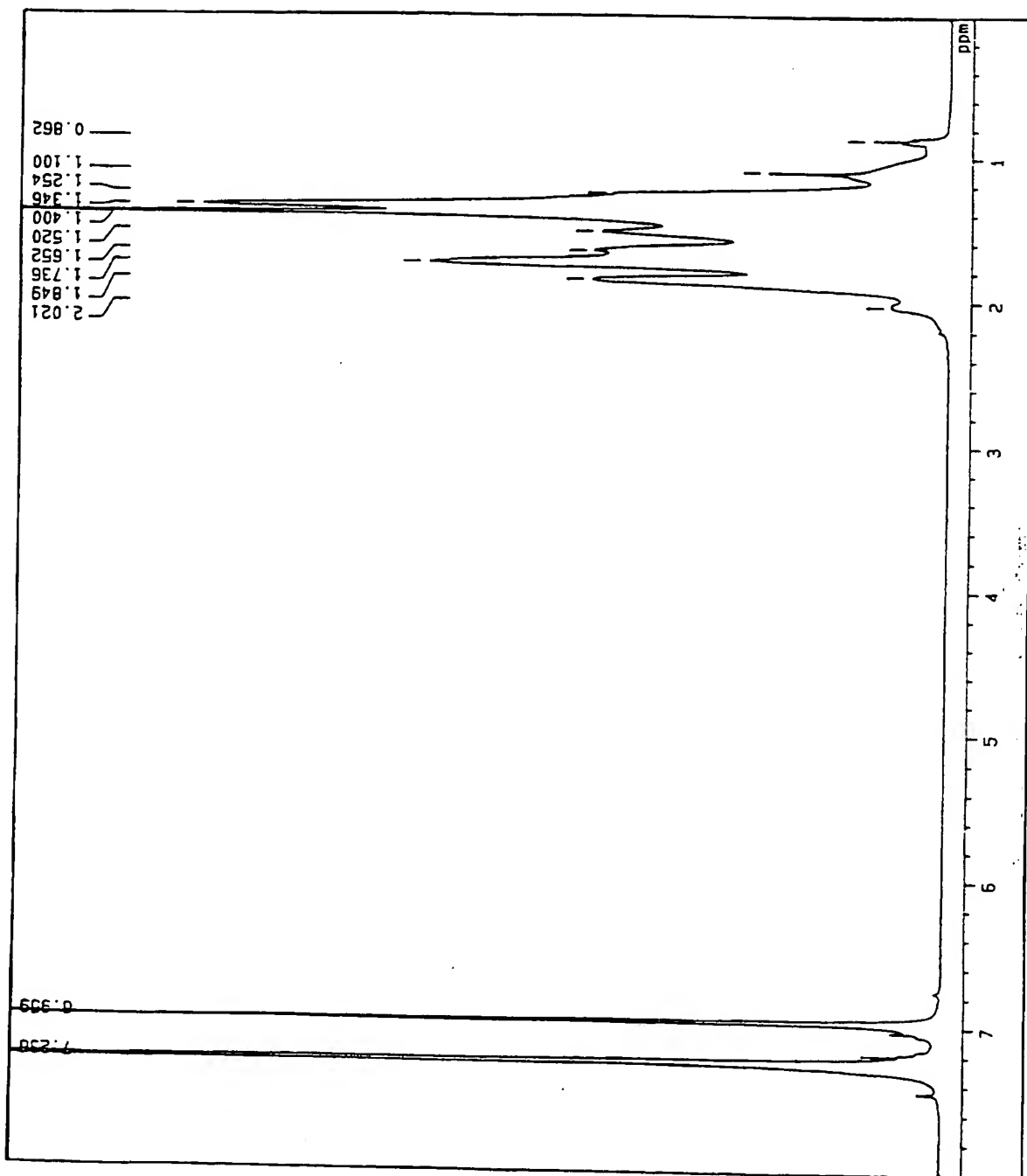


FIG. 16

## Specification

Title of the Invention

Improved cyclic conjugated diene polymer and  
method for producing the same

5                   Background of the inventionTechnical field

10                   The present invention relates to an improved  
cyclic conjugated diene polymer and a method for pro-  
ducing the same. More particularly, the present inven-  
tion is concerned with a novel cyclic conjugated diene  
polymer which comprises a main chain comprising at  
least one type of cyclic conjugated diene monomer unit,  
or comprising at least one type of cyclic conjugated  
diene monomer unit and a monomer unit derived from at  
15                   least one comonomer copolymerizable with the cyclic  
conjugated diene monomer, wherein the cyclic conjugated  
diene monomer units are bonded in the main chain by a  
1,2-bond and a 1,4-bond, and wherein the 1,2-bond/1,4-  
bond molar ratio is relatively high. The cyclic conju-  
20                   gated diene polymer of the present invention not only  
has a relatively narrow molecular weight distribution,  
but also is improved in respect of thermal properties  
and mechanical properties. The present invention is  
also concerned with a commercially advantageous method  
25                   for producing such an excellent cyclic conjugated diene



polymer, in which a unique catalyst is used.

Prior Art

In recent years, polymer chemistry has continuously made progress through various innovations in order to meet commercial demands which have become increasingly diversified. Especially in the field of polymers to be used as commercially important materials, extensive and intensive studies have been made toward developing polymers having more excellent thermal and mechanical properties. Various proposals have been made with respect to such polymers and methods for the production thereof.

For example, various proposals have been made with respect to conjugated diene polymers, such as a polybutadiene and a polyisoprene. The reason for this resides in the fact that the structures of the polymeric molecular chains of conjugated diene polymers can be relatively easily controlled so as to obtain polymer materials having desired properties. Some of the conjugated diene polymers produced by the techniques of such proposals have been widely used as commercially important materials.

However, in accordance with recent remarkable progress of the techniques in this field, there has been a strong demand for the development of polymer

materials having further improved properties, particularly excellent thermal properties (such as melting temperature, glass transition temperature and heat distortion temperature) and excellent mechanical properties (such as tensile modulus and flexural modulus).

As one of the most practical means for meeting such a demand, attempts have been made to develop a technique of improving the structures of the polymeric molecular chains of polymers of conjugated diene monomers (in homopolymerizing or copolymerizing not only a monomer having a relatively small steric hindrance, e.g., butadiene or isoprene, but also a monomer having a large steric hindrance, e.g., a cyclic conjugated diene monomer) so as to obtain polymer materials having excellent thermal and mechanical properties.

With respect to the homopolymerization or copolymerization of a monomer having a relatively small steric hindrance, e.g., butadiene or isoprene, catalyst systems having a polymerization activity which is satisfactory to a certain extent have been successfully developed. However, a catalyst system which exhibits a satisfactory polymerization activity in the homopolymerization or copolymerization of monomers having a large steric hindrance, e.g., a cyclic conjugated diene

monomer, has not yet been developed.

That is, by conventional techniques, even homopolymerization of a cyclic conjugated diene is difficult, so that a homopolymer having a desired high molecular weight cannot be obtained. Furthermore, for the purpose of obtaining a polymer having optimized thermal and mechanical properties so as to meet a wide variety of commercial needs, an attempt to copolymerize a cyclic conjugated diene with a monomer other than the cyclic conjugated diene has been made but was unsuccessful with the result that the products obtained are only oligomers having a low molecular weight.

As is apparent from the above, by any of the conventional techniques, it has been impossible to obtain cyclic conjugated diene polymers which have satisfactory properties. Therefore, it has been strongly desired to solve the above problems.

J. Am. Chem. Soc., 81, 448 (1959) discloses a cyclohexadiene homopolymer and a polymerization method therefor, which homopolymer is obtained by polymerizing 1,3-cyclohexadiene (a typical example of a cyclic conjugated diene monomer), using a composite catalyst comprised of titanium tetrachloride and triisobutylaluminum.

However, the polymerization method disclosed in

this prior art document is disadvantageous in that the use of a large amount of the catalyst is necessary, and the polymerization reaction must be conducted for a prolonged period of time, and that the obtained polymer has only an extremely low molecular weight. Therefore, the polymer obtained by the technique of this prior art document is of no commercial value.

Further, J. Polym. Sci., Pt. A, 2,3277 (1964) discloses methods for producing a cyclohexadiene homopolymer, in which the polymerization of 1,3-cyclohexadiene is conducted by various polymerization methods, such as radical polymerization, cationic polymerization, anionic polymerization and coordination polymerization.

In any of the methods disclosed in this prior art document, however, the polymers obtained have only an extremely low molecular weight. Therefore, the polymers obtained by the techniques of this prior art document are of no commercial value.

British Patent Application No. 1,042,625 discloses a method for producing a cyclohexadiene homopolymer, in which the polymerization of 1,3-cyclohexadiene is conducted using a large amount of an organolithium compound as a catalyst.

In the polymerization method disclosed in British

Patent Application No. 1,042,625, the catalyst must be used in an amount as large as 1 to 2 wt%, based on the total weight of the monomers. Therefore, this method is economically disadvantageous. Further, the polymer  
5 obtained by this method has only an extremely low molecular weight. Moreover, in this prior art document, there is no teaching or suggestion of obtaining a copolymer. Furthermore, the method of this prior art document has disadvantages in that the polymer obtained  
10 contains a large amount of catalyst residue, which is very difficult to remove from the polymer, so that the polymer obtained by this method is of no commercial value.

J. Polym. Sci., Pt. A, 3, 1553 (1965) discloses a  
15 cyclohexadiene homopolymer, which is obtained by polymerizing 1,3-cyclohexadiene using an organolithium compound as a catalyst. In this prior art document, the polymerization reaction must be continued for a period as long as 5 weeks, however, the polymer ob-  
20 tained has a number average molecular weight of only 20,000 or less.

Polym. Prepr. (Amer. Chem. Soc., Div. Polym. Chem.) 12, 402 (1971) teaches that when the polymeriza-  
25 tion of 1,3-cyclohexadiene is conducted using an organolithium compound as a catalyst, the upper limit of

the number average molecular weight of the cyclohexadiene homopolymer obtained is only from 10,000 to 15,000. Further, this document teaches that the reason for such a small molecular weight resides in the fact that, concurrently with the polymerization reaction, not only does a transfer reaction occur, which is caused by the abstraction of a lithium cation present in the polymer terminal, but also a reaction of elimination of lithium hydride occurs.

Die Makromolekulare Chemie., 163, 13 (1973) discloses a cyclohexadiene homopolymer which is obtained by polymerizing 1,3-cyclohexadiene using a large amount of an organolithium compound as a catalyst. However, the polymer obtained in this prior art document is an oligomer having a number average molecular weight of only 6,500.

European Polymer J., 9, 895 (1973) discloses a copolymer which is obtained by copolymerizing 1,3-cyclohexadiene with butadiene and/or isoprene, using a  $\pi$ -allylnickel compound as a polymerization catalyst. However, the polymer obtained in this prior art document is an oligomer having an extremely low molecular weight. Further, it has been reported that the polymer of this prior art document has a single glass transition temperature, which suggests that the polymer has a

random copolymer structure.

Kobunshi Ronbun-shu (Collection of theses concerning polymers), Vol. 34, No. 5,333 (1977) discloses a method for synthesizing a copolymer of 1,3-cyclohexadiene and acrylonitrile using zinc chloride as a polymerization catalyst. However, the alternating copolymer obtained in this prior art document is an oligomer having an extremely low molecular weight.

J. Polym. Sci., Polym. Chem. Ed., 20, 901 (1982) discloses a cyclohexadiene homopolymer which is obtained by polymerizing 1,3-cyclohexadiene using an organosodium compound as a catalyst. In this prior art document, the organosodium compound used is sodium naphthalene, and a radical anion derived from the sodium naphthalene forms a dianion which functions as a polymerization initiation site. This means that although the cyclohexadiene homopolymer reported in this document has an apparent number average molecular weight of 38,700, this homopolymer is actually only a combination of two polymeric molecular chains, each having a number average molecular weight of 19,350, which chains respectively extend from the polymerization initiation site in two different directions. Further, in the polymerization method disclosed in this document, the polymerization reaction needs to be

conducted at an extremely low temperature. Therefore, the technique of this prior art document is of no commercial value.

5 Makromol. Chem., 191, 2743 (1990) discloses a method for polymerizing 1,3-cyclohexadiene using a polystyryllithium as a polymerization initiator. In this prior art document, it is described that concurrently with the polymerization reaction, not only a transfer reaction, which is caused by the abstraction  
10 of a lithium cation present in the polymer terminal, but also a reaction of elimination of lithium hydride vigorously occurs. Further, it is reported that even though the polymerization is conducted using a polystyryllithium as a polymerization initiator, a styrene-  
15 cyclohexadiene block copolymer cannot be obtained at room temperature, and the product obtained is only a cyclohexadiene homopolymer. Further, in this prior art document, it is reported that when the polymerization reaction is conducted at  $-10^{\circ}\text{C}$ , a styrene-cyclohexa-  
20 diene block copolymer having a molecular weight of about 20,000 is obtained in extremely low yield, together with a cyclohexadiene homopolymer. However, the content of cyclohexadiene blocks in the obtained copolymer is extremely low. Further, this prior art document  
25 has no teaching or suggestion about not only a



block copolymer of cyclohexadiene with a chain conjugated diene monomer, but also a multiblock copolymer which is an at least-tri-block copolymer of cyclohexadiene, or a radial block copolymer of cyclohexadiene.

5           It has been reported that in any of the conventional techniques for producing a cyclohexadiene polymer by polymerization of 1,3-cyclohexadiene, the monomer units derived from 1,3-cyclohexadiene monomers are bonded in a main chain of the monomer only by a 1,3-  
10           bond, so that such a polymer has a glass transition temperature (T<sub>g</sub>) of only 89 °C or less.

          As can be easily understood from the above, by any of the conventional techniques, it has been impossible to obtain a cyclic conjugated diene copolymer which has  
15           excellent properties so that it can be satisfactorily used as an industrial material. Needless to say, a production process for such a cyclic conjugated diene copolymer is not known.

#### SUMMARY OF THE INVENTION

20           In these situations, the present inventors have made extensive and intensive studies with a view toward solving the above-mentioned problems. As a result, they have succeeded in developing a technique to produce an improved cyclic conjugated diene polymer comprising a main chain which is comprised partly or  
25

entirely of monomer units derived from the cyclic conjugated diene monomers. Specifically, by the use of a unique catalyst, it has become possible to synthesize the cyclic conjugated diene polymer by anion polymerization, preferably by living anion polymerization, of cyclic conjugated diene monomers under commercially advantageous conditions for a polymerization reaction, in which monomer units derived from the cyclic conjugated diene monomers are introduced, in a desired proportion and in a desired configuration, as a part or all of the monomer units constituting a main chain of the polymer. Further, in the polymer obtained by the technique of the present invention, the cyclic conjugated diene monomer units are bonded in a main chain of the polymer by a 1,2-bond and a 1,4-bond.

More specifically, the present inventors have found that when a mixture of a complex of at least one organometallic compound containing a metal belonging to Group IA of the Periodic Table (hereinafter, frequently referred to simply as "Group IA metal") with a complexing agent (a first complexing agent), and a further complexing agent (a second complexing agent) (wherein the first complexing agent and the second complexing agent may be the same or different) is used as a catalyst for polymerization of cyclic conjugated diene

monomers, not only does it become possible to suppress the occurrence of various disadvantageous phenomena inevitably accompanying the conventional techniques (such as a transfer reaction which is caused by the abstraction of a lithium cation present in the polymer terminal (which abstraction is caused by the cyclic conjugated diene monomer per se), and a reaction of elimination of lithium hydride), but also such a catalyst can exhibit excellent polymerization activity even under high temperature conditions, i.e., at about 40 °C to about 70 °C, so that a cyclic conjugated diene polymer can be commercially advantageously produced, wherein the cyclic conjugated diene monomers are bonded in the main chain of the polymer by a 1,2-bond and a 1,4-bond (in addition, the polymer has a relatively high 1,2-bond content), so that the polymer not only has a narrow molecular weight distribution, but also excellent thermal properties and mechanical properties. The present invention has been completed based on these novel findings.

Generally, in the field of organometallic chemistry, it has been well known that an organometallic compound containing Group IA metal, and a complexing agent, such as an amine, an ether and a metal alkoxide, together form a highly reactive complex. Therefore,

such a complex has been used as an effective reaction reagent in organic synthesis of monomers.

However, generally, in the field of polymer chemistry, it has been considered that a complex of an organometallic compound containing a Group IA metal is not preferable for use in a polymerization reaction, because the reactivity of the complex is likely to be extremely enhanced by ionization of the organometallic compound containing a Group IA metal, thus leading to an occurrence of disadvantageous side reactions, such as metalation.

However, as already mentioned above, by the present inventors, it has unexpectedly and surprisingly been found that when a mixture of a complex of at least one Group IA metal-containing organometallic compound with a first complexing agent, and a second complexing agent is used as a catalyst, the polymerization of cyclic conjugated diene monomers can advantageously proceed without the danger of occurrence of side reactions, such as metalation, wherein the structure of the complex in the above-mentioned catalyst can be maintained with thermal stability. Further, the present inventors have also found a surprising fact such that the use of a mixture of the complex of at least one Group IA metal-containing organometallic compound with

the first complexing agent, and the second complexing agent as a catalyst for producing a cyclic conjugated diene polymer is commercially advantageous not only in that it becomes possible to synthesize a cyclic conjugated diene polymer by living anion polymerization reaction of the cyclic conjugated diene monomers, but also in that the ratio of the cyclic conjugated diene monomer units which are bonded in the main chain of the cyclic conjugated diene polymer by 1,2-bonds is relatively high, so that the conjugated diene polymer has excellent thermal properties, such as a high glass transition temperature and a high heat distortion temperature.

Accordingly, it is an object of the present invention to provide an improved cyclic conjugated diene polymer which not only has a narrow molecular weight distribution, but also excellent thermal properties, such as high melting temperature, high glass transition temperature and high heat distortion temperature, and excellent mechanical properties, such as high tensile modulus and high flexural modulus.

It is another object of the present invention to provide a method for producing the above-mentioned excellent cyclic conjugated diene polymer, which method is advantageous not only in that it becomes possible to

polymerize cyclic conjugated diene monomers which have a large steric hindrance and therefore have been difficult to polymerize, but also in that the ratio of cyclic conjugated diene monomer units which are bonded in the main chain of the cyclic conjugated diene polymer by 1,2-bonds is relatively high.

The foregoing and other objects, features and advantages of the present invention will be apparent from the following detailed description and claims, taken in connection with the accompanying drawings.

#### BRIEF DESCRIPTION OF THE DRAWINGS

In the accompanying drawings:

FIG. 1(a) is a diagram showing the structure of a cyclohexadiene monomer unit having a 1,2-bond.

FIG. 1(b) is a diagram showing the structure of a cyclohexadiene monomer unit having a 1,4-bond.

FIG. 2 is a chart showing the 2-D (two-dimensional) NMR spectrum of the cyclohexadiene homopolymer obtained in Example 22, which was measured by H-H COSY method, in which not only cross peaks ascribed to hydrogen atoms bonded to a couple of carbon atoms of each cyclohexadiene monomer unit in the main chain of the cyclohexadiene homopolymer, wherein the couple of carbon atoms are bonded to each other by an olefin bond, but also cross peaks ascribed to hydrogen atoms

bonded to carbon atoms neighboring the above-mentioned couple of carbon atoms bonded to each other by an olefin bond, are observed;

FIG. 3 is a chart showing the 2-D (two-dimensional) NMR spectrum of the cyclohexadiene homopolymer obtained in Example 22, which was measured by H-H COSY method, in which cross peaks ascribed to hydrogen atoms bonded to a couple of carbon atoms of each cyclohexadiene monomer unit in the main chain of the cyclohexadiene homopolymer, wherein the couple of carbon atoms are bonded to each other by an olefin bond, are observed;

FIG. 4 is a chart showing the  $^1\text{H}$ -NMR spectrum of the complex having a Li [in n-butyl lithium (n-Buli)]/tetramethylethylenediamine (TMEDA) molar ratio of 4/2, obtained in Example 1;

FIG. 5 is a chart showing the  $^7\text{Li}$ -NMR spectrum of the complex having a Li (in n-Buli)/TMEDA molar ratio of 4/2, obtained in Example 1;

FIG. 6 is a chart showing the  $^1\text{H}$ -NMR spectrum of the complex-TMEDA mixture having a Li/TMEDA molar ratio of 4/5;

FIG. 7 is a chart showing the  $^7\text{Li}$ -NMR spectrum of the complex-TMEDA mixture having a Li/TMEDA molar ratio of 4/5;

FIG. 8 is a chart showing the  $^1\text{H}$ -NMR spectrum of n-Buli used in Comparative Example 8;

FIG. 9 is a chart showing the  $^7\text{L}$ -NMR spectrum of n-Buli used in Comparative Example 8;

5        FIG. 10 is a chart showing the  $^1\text{H}$ -NMR spectrum of the cyclic conjugated diene homopolymer of the present invention, obtained in Example 22;

10        FIG. 11 is a chart showing the  $^1\text{H}$ -NMR spectrum of the homopolymer of the present invention, comprised of saturated cyclic molecular units derived from cyclic conjugated diene monomers, which was obtained in Example 24;

15        FIG. 12 is a chart showing the  $^1\text{H}$ -NMR spectrum of the polycyclohexadiene-polyisoprene-polycyclohexadiene triblock copolymer of the present invention, obtained in Example 38;

20        FIG. 13 is a chart showing the  $^1\text{H}$ -NMR spectrum of the copolymer of the present invention, obtained by hydrogenation of the polycyclohexadiene-polyisoprene-polycyclohexadiene triblock copolymer in Example 44;

FIG. 14 is a chart showing the  $^1\text{H}$ -NMR spectrum of the polycyclohexadiene-polystyrene-polycyclohexadiene triblock copolymer of the present invention, obtained in Example 47;

25        FIG. 15 is a chart showing the  $^1\text{H}$ -NMR spectrum of

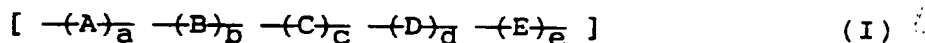


the polycyclohexadiene-polybutadiene-polycyclohexadiene triblock copolymer of the present invention, obtained in Example 57; and

FIG. 16 is a chart showing the  $^1\text{H}$ -NMR spectrum of the copolymer of the present invention, obtained by hydrogenation of the polycyclohexadiene-polystyrene-polycyclohexadiene triblock copolymer in Example 70.

#### DETAILED DESCRIPTION OF THE INVENTION

In one aspect of the present invention, there is provided a cyclic conjugated diene polymer comprising a main chain represented by the following formula (I):



wherein A to E are monomer units constituting the main chain in which monomer units A to E are arranged in any order, and a to e are, respectively, weight percentages of monomer units A to E, based on the total weight of monomer units A to E; wherein

A is selected from the class consisting of cyclic conjugated diene monomer units,  
B is selected from the class consisting of chain conjugated diene monomer units,  
C is selected from the class consisting of vinyl aromatic monomer units,

D is selected from the class consisting of polar monomer units, and

E is selected from the class consisting of an ethylene monomer unit and  $\alpha$ -olefin monomer units;

5

wherein:

a to e satisfy the following requirements:

$$a + b + c + d + e = 100,$$

$$0.1 \leq a \leq 100,$$

10

$$0 \leq b < 100,$$

$$0 \leq c < 100,$$

$$0 \leq d < 100, \text{ and}$$

$$0 \leq e < 100; \text{ and}$$

15

wherein the A monomer units are bonded in the main chain by a 1,2-bond and a 1,4-bond,

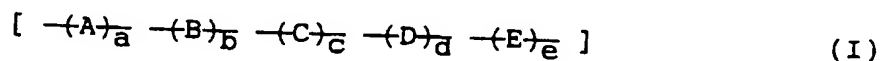
wherein the molar ratio of the 1,2-bond to the 1,4-bond is from 40/60 to 90/10,

the cyclic conjugated diene polymer having a number average molecular weight of 500 to 5,000,000.

20

In another aspect of the present invention, there is provided a method for producing a cyclic conjugated diene polymer comprising a main chain represented by the following formula (I):

25



wherein A to E are monomer units constituting the main chain in which monomer units A to E are arranged in any order, and a to e are, respectively, weight percentages of monomer units A to E, based on the total weight of monomer units A to E; wherein

A is selected from the class consisting of cyclic conjugated diene monomer units,

B is selected from the class consisting of chain conjugated diene monomer units,

C is selected from the class consisting of vinyl aromatic monomer units,

D is selected from the class consisting of polar monomer units, and

E is selected from the class consisting of an ethylene monomer unit and  $\alpha$ -olefin monomer units; and

wherein:

a to e satisfy the following requirements:

$$a + b + c + d + e = 100,$$

$$0.1 \leq a \leq 100,$$

$$0 \leq b < 100,$$

$$0 \leq c < 100,$$

$$0 \leq d < 100, \text{ and}$$

$$0 \leq e < 100;$$

the cyclic conjugated diene polymer having a number average molecular weight of 500 to 5,000,000, which comprises:

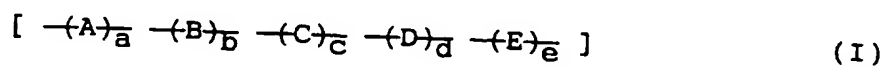
5 providing a complex of at least one organometallic compound containing a metal belonging to Group IA of the Periodic Table with at least one first complexing agent, and

10 polymerizing at least one cyclic conjugated diene monomer, or at least one cyclic conjugated diene monomer and at least one comonomer copolymerizable therewith in the presence of a catalyst comprising a mixture of the complex and at least one second complexing agent,

15 the at least one comonomer being selected from the class consisting of chain conjugated diene monomers, vinyl aromatic monomers, polar monomers, an ethylene monomer, and  $\alpha$ -olefin monomers.

20 For easy understanding of the present invention, the essential features and various embodiments of the present invention are enumerated below.

1. A cyclic conjugated diene polymer comprising a main chain represented by the following formula (I):



25 wherein A to E are monomer units constituting the

main chain in which monomer units A to E are arranged in any order, and a to e are, respectively, weight percentages of monomer units A to E, based on the total weight of monomer units A to E;

5 wherein

A is selected from the class consisting of cyclic conjugated diene monomer units,

B is selected from the class consisting of chain conjugated diene monomer units,

10 C is selected from the class consisting of vinyl aromatic monomer units,

D is selected from the class consisting of polar monomer units, and

15 E is selected from the class consisting of an ethylene monomer unit and  $\alpha$ -olefin monomer units;

wherein:

a to e satisfy the following requirements:

$$a + b + c + d + e = 100,$$

20  $0.1 \leq a \leq 100,$

$$0 \leq b < 100,$$

$$0 \leq c < 100,$$

$$0 \leq d < 100, \text{ and}$$

$$0 \leq e < 100; \text{ and}$$

25 wherein the A monomer units are bonded in the

main chain by a 1,2-bond and a 1,4-bond,  
wherein the molar ratio of the 1,2-bond to  
the 1,4-bond is from 40/60 to 90/10,  
the cyclic conjugated diene polymer having a  
5 number average molecular weight of 500 to 5,000,000.

2. The cyclic conjugated diene polymer according to  
item 1 above, which is a block copolymer.
- 10 3. The cyclic conjugated diene polymer according to  
item 1 or 2 above, which has a glass transition temper-  
ature (T<sub>g</sub>) of 150 °C or more.
- 15 4. The cyclic conjugated diene polymer according to  
item 2 above, wherein the block copolymer contains a  
polymer block having a glass transition temperature  
(T<sub>g</sub>) of 150 °C or more.
- 20 5. The cyclic conjugated diene polymer according to  
any one of items 2 to 4 above, which is an at  
least-tri-block copolymer.
- 25 6. The cyclic conjugated diene polymer according to  
any one of items 2 to 5 above, which is a block copoly-  
mer having a polymer block containing at least two A

monomer units.

7. The cyclic conjugated diene polymer according to any one of items 2 to 5 above, which is a block copolymer having a polymer block consisting of at least two A monomer units.

8. The cyclic conjugated diene polymer according to any one of items 2 to 4 above, which is an at least-di-block copolymer comprising at least one polymer block consisting of at least two A monomer units, and at least one polymer block consisting of monomer units of at least one type selected from the group consisting of the B to the E monomer units.

9. The cyclic conjugated diene polymer according to any one of items 2 to 4 above, which is a diblock copolymer comprising one X polymer block containing at least one A monomer unit, and one Y polymer block comprised mainly of monomer units of at least one type selected from the B and the E monomer units, wherein the weight ratio of the X block to the Y block is from 1/99 to 99/1.

10. The cyclic conjugated diene polymer according to

item 5 above, which is an at least-tri-block copolymer comprising at least two X blocks each containing at least one A monomer unit, and at least one Y block comprised mainly of monomer units of at least one type selected from the B and the E monomer units, wherein the weight ratio of the at least two X blocks to the at least one Y block is from 1/99 to 99/1.

11. The cyclic conjugated diene polymer according to item 5 above, which is a triblock copolymer comprising two X blocks containing at least one A monomer unit, and one Y block comprised mainly of monomer units of at least one type selected from the B and the E monomer units.

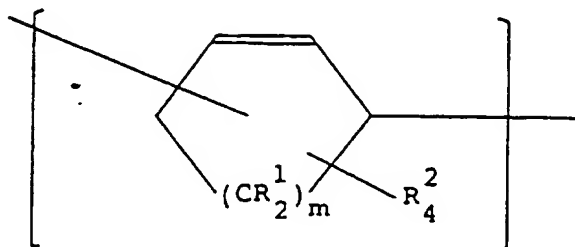
12. The cyclic conjugated diene polymer according to item 10 above, wherein the at least-tri-block copolymer has a configuration represented by a formula selected from the group consisting of  $X - (Y - X)_p$ ,  $(X - Y)_q$ ,  $Y - (X - Y)_q$ ,  $[(Y - X)_{\overline{p}}]_{\overline{q}}$ ,  $[(X - Y)_{\overline{p}}]_{\overline{q}}$ ,  $[(Y - X)_{\overline{p}} - Y]_{\overline{q}}$ , and  $[(X - Y)_{\overline{p}} - X]_{\overline{q}}$  in which X and Y are as defined above, p is an integer of 1 or more, and q is an integer of 2 or more.

13. The cyclic conjugated diene polymer according to



any one of items 1 to 12 above, wherein the A monomer unit is selected from the class consisting of monomer units represented by the following formula (II):

5



(II)

10

wherein  $m$  is an integer of from 1 to 4, each  $R^1$  independently represents a hydrogen atom, a halogen atom, a  $C_1$ - $C_{20}$  alkyl group, a  $C_2$ - $C_{20}$  unsaturated aliphatic hydrocarbon group, a  $C_5$ - $C_{20}$  aryl group, a  $C_3$ - $C_{20}$  cycloalkyl group, a  $C_4$ - $C_{20}$  cyclodienyl group or a 5 to 10-membered heterocyclic group having at least one nitrogen, oxygen or sulfur atom as a heteroatom, and each  $R^2$  independently represents a hydrogen atom, a halogen atom, a  $C_1$ - $C_{20}$  alkyl group, a  $C_2$ - $C_{20}$  unsaturated aliphatic hydrocarbon group, a  $C_5$ - $C_{20}$  aryl group, a  $C_3$ - $C_{20}$  cycloalkyl group, a  $C_4$ - $C_{20}$

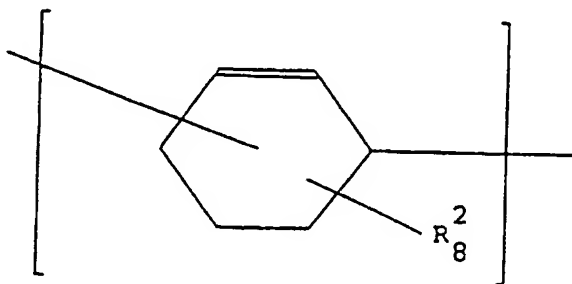
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cyclodienyl group or a 5 to 10-membered heterocyclic group having at least one nitrogen, oxygen or sulfur atom as a heteroatom, or each  $R^2$  independently represents a bond or a group such that two  $R^2$  groups together form a bridge represented by the formula  $-(CR_2^3)_n$  in which  $R^3$  has the same meaning as defined for  $R^1$  and  $n$  is an integer of from 1 to 10.

14. The cyclic conjugated diene polymer according to item 13 above, wherein the A monomer unit is selected from the class consisting of monomer units represented by the following formula (III):



(III)

wherein each  $R^2$  is as defined for formula (II).

15. The cyclic conjugated diene polymer according to item 13 above, wherein the A monomer unit is at least one member selected from the class consisting of a 1,3-cyclopentadiene monomer unit, a 1,3-cyclohexadiene monomer unit, a 1,3-cyclooctadiene monomer unit, and derivatives thereof.
16. A cyclic conjugated diene polymer according to item 14 above, wherein the A monomer unit is a 1,3-cyclohexadiene monomer unit or a derivative thereof.
17. The cyclic conjugated diene polymer according to item 14 above, wherein the A monomer unit is a 1,3-cyclohexadiene monomer unit.
18. A polymer produced by subjecting a cyclic conjugated diene polymer of any one of items 1 to 17 above to at least one reaction selected from the group consisting of hydrogenation, halogenation, hydrohalogenation, alkylation, arylation, a ring-opening reaction and dehydrogenation.
19. A method for producing a cyclic conjugated diene polymer comprising a main chain represented by the following formula (I):

$$[ -(A)_a -(B)_b -(C)_c -(D)_d -(E)_e ] \quad (I)$$

wherein A to E are monomer units constituting the main chain in which monomer units A to E are arranged in any order, and a to e are, respectively, weight percentages of monomer units A to E, based on the total weight of monomer units A to E; wherein

A is selected from the class consisting of cyclic conjugated diene monomer units,

B is selected from the class consisting of chain conjugated diene monomer units,

C is selected from the class consisting of vinyl aromatic monomer units,

D is selected from the class consisting of polar monomer units, and

E is selected from the class consisting of an ethylene monomer unit and  $\alpha$ -olefin monomer units; and

wherein:

a to e satisfy the following requirements:

$$a + b + c + d + e = 100,$$

$$0.1 \leq a \leq 100,$$

$$0 \leq b < 100,$$

$$0 \leq c < 100,$$

$0 \leq d < 100$ , and

$0 \leq e < 100$ ;

the cyclic conjugated diene polymer having a number average molecular weight of 500 to 5,000,000,

5 which comprises:

providing a complex of at least one organometallic compound containing a metal belonging to Group IA of the Periodic Table with at least one first complexing agent, and

10 polymerizing at least one cyclic conjugated diene monomer, or at least one cyclic conjugated diene monomer and at least one comonomer copolymerizable therewith, in the presence of a catalyst comprising a mixture of the complex and at least one second complexing agent,

15 the at least one comonomer being selected from the class consisting of chain conjugated diene monomers, vinyl aromatic monomers, polar monomers, an ethylene monomer, and  $\alpha$ -olefin monomers.

20 20. The method according to item 19 above, wherein each of the at least one first complexing agent and the at least one second complexing agent is independently an organic compound containing at least one element  
25 selected from the group consisting of oxygen (O),

nitrogen (N), sulfur (S) and phosphorus (P).

21. The method according to item 19 above, wherein each of the at least one first complexing agent and the at least one second complexing agent is independently an organic compound selected from the group consisting of an ether, a metal alkoxide, an amine and a thioether.
22. The method according to item 19 above, wherein each of the at least one first complexing agent and the at least one second complexing agent is independently an ether or an amine.
23. The method according to item 19 above, wherein each of the at least one first complexing agent and the at least one second complexing agent is independently an amine.
24. The method according to item 19 above, wherein each of the at least one first complexing agent and the at least one second complexing agent is independently a diamine.
25. The method according to item 19 above, wherein

each of the at least one first complexing agent and the at least one second complexing agent is independently an aliphatic diamine.

- 5        26. The method according to item 19 above, wherein each of the at least one first complexing agent and the at least one second complexing agent is independently a tertiary amine.
- 10       27. The method according to item 24 above, wherein the diamine compound is selected from the group consisting of tetramethylethylenediamine (TMEDA) and diazabicyclo[2,2,2]octane (DABCO).
- 15       28. The method according to any of items 19 to 27 above, wherein the at least one organometallic compound containing a metal belonging to Group IA of the Periodic Table is an organolithium compound.
- 20       29. The method according to item 19 above, wherein the at least one organometallic compound containing a metal belonging to Group IA of the Periodic Table is an organolithium compound selected from the group consisting of normal butyllithium (n-BuLi), secondary butyllithium (s-BuLi) and tertiary butyllithium (t-BuLi),
- 25

and each of the at least one first complexing agent and the at least one second complexing agent is independently selected from the group consisting of tetramethylethylenediamine (TMEDA) and diazabicyclo[2,2,2]octane (DABCO).

30. The method according to any of items 19 to 29 above, wherein the complex is one which is prepared by reacting the at least one organometallic compound containing a metal belonging to Group IA of the Periodic Table with the at least one first complexing agent in a molar ratio represented by the following formula:

$$A_1/B_1 = 200/1 \text{ to } 1/100$$

wherein  $A_1$  represents the molar amount of the Group IA metal contained in the at least one organometallic compound used for the reaction, and  $B_1$  represents the molar amount of the at least one first complexing agent used for the reaction.

31. The method according to any one of items 19 to 29 above, wherein the complex is comprised of the at least one organometallic compound containing a metal belonging to Group IA metal of the Periodic Table and the at least one first complexing agent in molar ratio repre-



sented by the following formula:

$$A_2/B_2 = 1/0.25 \text{ to } 1/1$$

5 wherein A<sub>2</sub> represents the molar amount of the Group IA metal contained in the at least one organometallic compound constituent of the complex, and B<sub>2</sub> represents the amount of the at least one first complexing agent constituent of the complex.

10 32. The method according to any one of items 19 to 29 above, wherein, in the catalyst, the at least one organometallic compound, the at least one first complexing agent and the at least one second complexing agent are present in a molar ratio relationship represented by the following formula:

$$A_3/B_3 = 100/1 \text{ to } 1/200$$

15 wherein A<sub>3</sub> represents the molar amount of the Group IA metal contained in the at least one organometallic compound, and B<sub>3</sub> represents the total molar amount of the at least one first complexing agent and the at least one second complexing agent.

20 In the present invention, the monomer units of the polymer are named in accordance with a nomenclature such that the names of the original monomers from which

25

the monomer units are derived, as such, are used with the term "unit" attached thereto. For example, the term "cyclic conjugated diene monomer unit" means a monomer unit which is formed in a polymer obtained by the polymerization of a cyclic conjugated diene monomer and which has a molecular structure such that a cycloolefin corresponding to the cyclic conjugated diene monomer is bonded at two carbon atoms of a skeleton thereof. Further, the term "cyclic olefin monomer unit" means a monomer unit which is formed in a polymer obtained by the polymerization of a cyclic olefin monomer and which has a molecular structure such that a cycloalkane corresponding to the cyclic olefin monomer is bonded at two carbon atoms of a skeleton thereof.

In the present invention, the cyclic conjugated diene polymer is a polymer comprising a main chain which is comprised partly or entirely of monomer units derived from cyclic conjugated diene monomers and/or monomer units derived from the above monomer units.

Representative examples of cyclic conjugated diene polymers of the present invention include a polymer comprising a main chain which is comprised solely of at least one monomer unit selected from the class consisting of cyclic conjugated diene monomer units, and a polymer comprising a main chain which is comprised of

at least one monomer unit selected from the class consisting of cyclic conjugated diene monomer units and a monomer unit derived from at least one comonomer copolymerizable with the conjugated diene monomer.

5           More specific examples of the cyclic conjugated diene polymer of the present invention include a homopolymer of a cyclic conjugated diene monomer, a copolymer of at least two types of cyclic conjugated diene monomers, and a copolymer of at least one cyclic conjugated diene monomer and at least one comonomer copolymerizable with the cyclic conjugated diene monomer.

10

          The preferred examples of cyclic conjugated diene polymers of the present invention include a polymer comprising a main chain which is comprised of at least one monomer unit selected from the class consisting of cyclic conjugated diene monomer units having a cyclohexene ring in the molecular structure thereof and cyclic conjugated diene monomer units having a cyclohexene ring in the molecular structure thereof.

15

20           In another aspect of the present invention, there is provided a polymer produced by subjecting the cyclic conjugated diene polymer of the present invention to at least one reaction selected from the group consisting of hydrogenation, halogenation, hydrohalogenation, alkylation, arylation, a ring-opening reaction and dehy-

25

drogenation.

In the present invention, the term "cyclic conjugated diene monomer" means a cyclic conjugated diene having an at least-5-membered carbocyclic structure.

5 It is preferred that the cyclic conjugated diene monomer be a cyclic conjugated diene having a 5 to 8-membered carbocyclic structure.

10 It is more preferred that the cyclic conjugated diene monomer be a cyclic conjugated diene having a 6-membered carbocyclic structure.

Examples of cyclic conjugated diene monomers include 1,3-cyclopentadiene, 1,3-cyclohexadiene, 1,3-cyclooctadiene, and derivatives thereof. Preferred examples of cyclic conjugated diene monomers include 15 1,3-cyclohexadiene and 1,3-cyclohexadiene derivatives. Of these, 1,3-cyclohexadiene is most preferred.

In the present invention, as examples of comonomers copolymerizable with the cyclic conjugated diene monomer, there can be mentioned monomers which can be 20 polymerized by anionic polymerization.

Examples of such monomers include chain conjugated diene monomers, such as 1,3-butadiene, isoprene, 2,3-dimethyl-1,3-butadiene, 1,3-pentadiene, 1,3-hexadiene and derivatives thereof; vinyl aromatic monomers, such 25 as styrene,  $\alpha$ -methylstyrene, o-methylstyrene, p-me-

thylstyrene, p-tert-butylstyrene, 1,3-dimethylstyrene, divinylbenzene, vinyl naphthalene, vinylanthracene, 1,1-diphenylethylene, m-diisopropenylbenzene, vinylpyridine and derivatives thereof; polar vinyl monomers, such as methyl methacrylate, methyl acrylate, acrylonitrile, methyl vinyl ketone and methyl  $\alpha$ -cyanoacrylate; polar monomers, such as ethylene oxide, propylene oxide, cyclohexene oxide, lactone, lactam and cyclosiloxane; ethylene monomer; and  $\alpha$ -olefin monomers.

Each of these monomers can be used individually or in combination.

In the present invention, a copolymer of the cyclic conjugated diene monomer with the above-mentioned comonomer may be of any configuration.

For example, the copolymer may be a block copolymer, such as a diblock, a triblock, a tetrablock, a multiblock, a radial block, an asymmetry radial block, a graft block, a star block or a comb block copolymer, a graft copolymer, a taper copolymer, a random copolymer or an alternating copolymer.

In the cyclic conjugated diene polymer of the present invention, the monomer unit derived from at least one comonomer copolymerizable with the cyclic conjugated diene monomer may be a monomer unit which is formed by a post-polymerization treatment, such as

hydrogenation, halogenation, alkylation, arylation or the like.

In the cyclic conjugated diene polymer of the present invention, the content of the cyclic conjugated diene monomer unit is not particularly limited and may vary depending on the intended use of the polymer. However, the content of the cyclic conjugated diene monomer unit is generally within the range of from 0.1 to 100 wt%, preferably from 0.5 to 100 wt%, more preferably from 1 to 100 wt%, based on the weight of the main chain of the cyclic conjugated diene polymer.

Further, for obtaining a cyclic conjugated diene polymer of the present invention which can be used in a field where the polymer is required to have high thermal and mechanical properties, it is recommended that the content of the cyclic conjugated diene monomer unit in the cyclic conjugated diene polymer be within the range of from 5 to 100 wt%, more preferably from 10 to 100 wt%, most preferably from 15 to 100 wt%, based on the weight of the main chain of the cyclic conjugated diene polymer.

In the present invention, the cyclic conjugated diene polymer can be produced by living anionic polymerization, so that the molecular weight of the polymer can be appropriately controlled.

From the viewpoint of productivity in the commercial scale production of such a polymer, it is recommended that the number average molecular weight of the polymer be within the range of from 500 to 5,000,000.

5           For example, when the polymer is used as a functional material, the number average molecular weight of the polymer is within the range of from 500 to 2,000,000 preferably from 1,000 to 1,000,000, more preferably from 2,000 to 800,000, most preferably from  
10           3,000 to 500,000.

          On the other hand, when the polymer is used as a structural material, the number average molecular weight of the polymer is generally within the range of from 20,000 to 5,000,000, preferably from 30,000 to  
15           4,000,000, more preferably from 40,000 to 3,000,000, still more preferably from 40,000 to 2,000,000, most preferably from 40,000 to 1,000,000.

          With respect to the cyclic conjugated diene polymer of the present invention, for controlling the  
20           molecular weight of the polymer or for obtaining it in the form of a star shaped polymer, it can assume a configuration such that the terminals of a plurality of polymeric molecular chains are bonded using a conventional at least-bi-functional coupling agent, such as  
25           dimethyldichlorosilane, methyltrichlorosilane, dime-

thyldibromosilane, methyltribromosilane, titanocene  
dichloride, methylene chloride, methylene bromide,  
chloroform, carbon tetrachloride, silicon tetrachlo-  
ride, titanium tetrachloride, tin tetrachloride, an  
5 epoxidized soybean oil, or an ester.

In the present invention, the number average  
molecular weight ( $\overline{Mn}$ ) is measured by gel permeation  
chromatography, using a calibration curve obtained with  
respect to standard polystyrene samples.

10 In the present invention, the  $\overline{Mw}/\overline{Mn}$  value  
(criterion of the molecular weight distribution) of the  
cyclic conjugated diene polymer is within the range of  
from 1.01 to 10, preferably from 1.03 to 7.0, more  
preferably from 1.03 to 5.0, furthermore preferably  
15 from 1.03 to 2.50, most preferably from 1.03 to 2.00.

In the cyclic conjugated diene polymer of the  
present invention, the polymeric molecular chain there-  
of has a structure such that the monomer units A are  
bonded by a 1,2-bond or a 1,4-bond. The content of  
20 each of the 1,2-bond and the 1,4-bond can be measured  
by  $^1\text{H-NMR}$ . In the present invention, it is necessary  
that the polymer have a 1,2-bond content of from 40 to  
90 mol%, based on the total mol of the 1,2-bond and the  
1,4-bond.

25 When the cyclic conjugated diene polymer has a



1,2-bond content within the above-mentioned range, such a cyclic conjugated diene polymer advantageously has a high glass transition temperature ( $T_g$ ), which, therefore, has excellent thermal properties.

5           When the 1,2-bond content of the polymer is lower than 40 mol%, the  $T_g$  value of the polymer disadvantageously becomes low, so that the polymer has poor thermal properties. On the other hand, when the 1,2-bond content of the polymer is higher than 90 mol%, the  
10        $T_g$  value of the polymer becomes too high, so that the difference between the decomposition temperature of the polymer and the temperature usable for molding or processing of the polymer becomes small.

          Further, from the viewpoint of properties, productivity, moldability and processability of the cyclic  
15       conjugated diene polymer of the present invention, it is preferred that the polymer have a 1,2-bond content of from 40 to 85 mol%, more preferably from 40 to 80 mol%, most preferably 40 to 70 mol%, based on the total  
20       number of moles of the 1,2-bond and the 1,4-bond.

          Further, for obtaining a cyclic conjugated diene polymer having excellent thermal and mechanical properties, it is most preferred that the cyclic conjugated diene polymer have a 1,2-bond content of from 40 to 90  
25       mol% and a  $T_g$  value of 150 °C or more.

When the cyclic conjugated diene polymer of the present invention is a cyclic conjugated diene block copolymer containing a plurality of different polymer blocks in the polymeric molecular chain thereof, the block copolymer may contain a polymer block comprised of monomer units derived solely from at least one type of cyclic conjugated diene monomer, a polymer block comprised of a monomer unit derived from at least one type of cyclic conjugated diene monomer and a monomer unit derived from at least one type of comonomer copolymerizable with the cyclic conjugated diene, or a polymer block comprised of monomer units derived solely from at least one comonomer copolymerizable with the cyclic conjugated diene monomer. For attaining various purposes, various types of polymer blocks can be designed and polymerized. By an appropriate choice and combination of such polymer blocks, a cyclic conjugated diene block copolymer having suitable properties for the intended use can be obtained.

In the present invention, when a part or all of a polymer block is comprised of monomer units selected from the class consisting of cyclic conjugated diene monomer units, it is necessary that the polymer block contain at least 1 cyclic conjugated diene monomer unit. Further, in this case, it is recommended that

the polymer block contain a contiguous arrangement of at least 2 cyclic conjugated diene monomer units, preferably 5 or more cyclic conjugated diene monomer units, more preferably 10 or more cyclic conjugated diene monomer units, from the viewpoint of improvement of thermal and mechanical properties of the cyclic conjugated diene block copolymer of the present invention.

As a method for producing a cyclic conjugated diene block copolymer of the present invention, there can be mentioned a method which comprises preparing a block unit polymer comprised of monomer units derived from at least one type of cyclic conjugated diene monomer, a block unit polymer comprised of monomer units derived from at least one cyclic conjugated diene monomer and a monomer unit derived from at least one type of comonomer copolymerizable with the cyclic conjugated diene monomer, and a block unit polymer comprised of monomer units derived from at least one type of comonomer copolymerizable with the cyclic conjugated diene monomer; choosing an appropriate combination of these block unit polymers; and polymerization-bonding the combination of block unit polymers together, thereby obtaining a cyclic conjugated diene block copolymer having suitable properties for the

intended use of the polymer. If desired, the cyclic conjugated diene block copolymer can be subjected to at least one reaction selected from the group consisting of hydrogenation, halogenation, hydrohalogenation, alkylation, arylation, a ring-opening reaction and dehydrogenation.

Specific examples of preferred modes of the method of the present invention include the following modes.

One mode of the method comprises the steps of forming by polymerization a block unit polymer containing a monomer unit derived from at least one type of cyclic conjugated diene monomer, or a block unit polymer derived solely from the cyclic conjugated diene monomer; and polymerizing the block unit polymer with at least one type of comonomer copolymerizable with the cyclic conjugated diene monomer, wherein the comonomer is successively bonded to one or both terminals of the block unit polymer by polymerization. If desired, the block copolymer obtained may be subjected to at least one reaction selected from the group consisting of hydrogenation, halogenation, hydrohalogenation, alkylation, arylation, a ring-opening reaction and dehydrogenation.

Another mode of the method comprises the steps of polymerizing at least one type of comonomer copolymer-

izable with a cyclic conjugated diene monomer to obtain a block unit polymer; and polymerizing the block unit polymer with at least one cyclic conjugated diene monomer, and optionally with at least one type of comonomer copolymerizable with the cyclic conjugated diene monomer, wherein the cyclic conjugated diene monomer and the optional comonomer are successively bonded to one or both terminals of the block unit polymer by polymerization. If desired, the block copolymer obtained may be subjected to at least one reaction selected from the group consisting of hydrogenation, halogenation, hydrohalogenation, alkylation, arylation, a ring-opening reaction and dehydrogenation.

A further mode of the method comprises the steps of forming by polymerization a block unit polymer containing a monomer unit derived from at least one cyclic conjugated diene monomer, or a block unit polymer derived solely from the cyclic conjugated diene monomer; polymerizing the block unit polymer with at least one type of comonomer copolymerizable with the cyclic conjugated diene monomer to obtain a polymer; and successively bonding to the polymer by polymerization a block unit polymer containing a monomer unit derived from at least one cyclic conjugated diene monomer or a block unit polymer derived solely from the

cyclic conjugated diene monomer. If desired, the block copolymer obtained may be subjected at least one reaction selected from the group consisting of hydrogenation, halogenation, hydrohalogenation, alkylation, arylation, a ring-opening reaction and dehydrogenation.

Still a further mode of the method comprises the steps of polymerizing at least one type of comonomer copolymerizable with the cyclic conjugated diene monomer to obtain a block unit polymer; polymerizing the block unit polymer with a block unit polymer containing a monomer unit derived from at least one cyclic conjugated diene monomer or a block unit polymer derived solely from the cyclic conjugated diene polymer; and successively bonding to the resultant polymer by polymerization at least one type of comonomer copolymerizable with the cyclic conjugated diene monomer. If desired, the block copolymer obtained may be subjected to at least one reaction selected from the group consisting of hydrogenation, halogenation, hydrohalogenation, alkylation, arylation, a ring-opening reaction and dehydrogenation.

Still a further mode of the method comprises polymerizing at least one cyclic conjugated diene monomer with at least one type of comonomer copolymerizable with the cyclic conjugated diene monomer, where-

in the at least one comonomer has a different polymerization rate from that of the cyclic conjugated diene monomer, to thereby obtain a taper block copolymer. If desired, the block copolymer obtained may be subjected to at least one reaction selected from the group consisting of hydrogenation, halogenation, hydrohalogenation, alkylation, arylation, a ring-opening reaction and dehydrogenation.

Still a further mode of the method comprises the steps of forming by polymerization a block unit polymer containing a monomer unit derived from at least one cyclic conjugated diene monomer or a block unit polymer derived only from the cyclic conjugated diene monomer; polymerizing the block unit polymer with at least one type of comonomer copolymerizable with the cyclic conjugated diene monomer to obtain a polymer; and bonding the terminals of the polymeric molecular chain of the polymer using a conventional at least-bi-functional coupling agent (such as dimethyldichlorosilane, methyltrichlorosilane, dimethyldibromosilane, methyltribromosilane, titanocene dichloride, methylene chloride, methylene bromide, chloroform, carbon tetrachloride, silicon tetrachloride, titanium tetrachloride, tin tetrachloride, an epoxidized soybean oil, or an ester). If desired, the block copolymer obtained may

be subjected to at least one reaction selected from the group consisting of hydrogenation, halogenation, hydrohalogenation, alkylation, arylation, a ring-opening reaction and dehydrogenation.

5           Still a further mode of the method comprises polymerizing a cyclic conjugated diene monomer and at least one type of comonomer copolymerizable with the cyclic conjugated diene monomer, wherein the ratio of the cyclic conjugated diene monomer to the at least one  
10           comonomer is not unity. If desired, the block copolymer obtained may be subjected to at least one reaction selected from the group consisting of hydrogenation, halogenation, hydrohalogenation, alkylation, arylation, a ring-opening reaction and dehydrogenation.

15           Still a further mode of the method comprises the steps of forming by polymerization a block unit polymer containing a monomer unit derived from at least one cyclic conjugated diene monomer or a block unit polymer derived only from the cyclic conjugated diene monomer,  
20           wherein the polymerization is conducted until a desired certain conversion is achieved, so that a certain amount of a cyclic conjugated diene monomer remains unreacted; and polymerizing the above-mentioned certain amount of the unreacted cyclic conjugated diene mono-  
25           mer, to thereby obtain a block copolymer. If desired,



the block copolymer obtained may be subjected to at least one reaction selected from the group consisting of hydrogenation, halogenation, hydrohalogenation, alkylation, arylation, a ring-opening reaction and  
5 dehydrogenation.

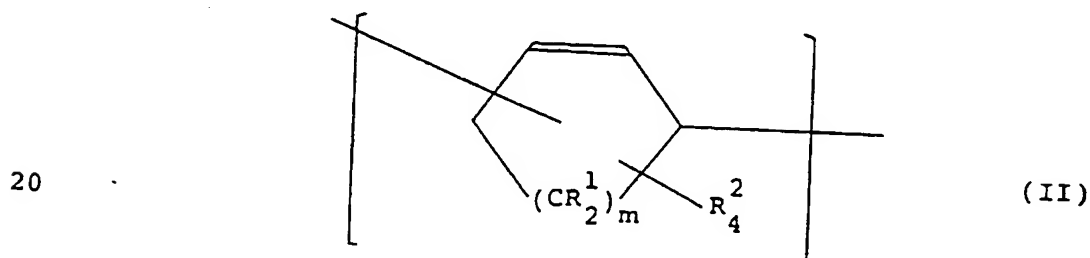
In the present invention, the block unit polymer comprised of at least one monomer unit selected from the class consisting of cyclic conjugated diene monomer units may further comprise a monomer unit derived from  
10 at least one comonomer copolymerizable with the cyclic conjugated diene monomer.

Further, in the present invention, the block unit polymer comprised of a monomer unit derived from at least one comonomer copolymerizable with the cyclic  
15 conjugated diene monomer may further comprise at least one monomer unit selected from the class consisting of cyclic conjugated diene monomer units.

In the present invention, with respect to monomer units derived from at least one type of cyclic conjugated diene monomer and to polymer blocks comprised of  
20 such monomer units, it is most preferred to use, respectively, a monomer unit comprised of a cyclohexene ring and a polymer block comprising a monomer unit comprised of a cyclohexene ring or consisting of monomer units each comprised of a cyclohexene ring. If  
25

desired, the monomer unit and the polymer block may be a monomer unit and a polymer block which are obtained by subjecting the above-mentioned monomer unit and the above-mentioned block unit to at least one reaction selected from the group consisting of hydrogenation, halogenation, hydrohalogenation, alkylation, arylation, a ring-opening reaction and dehydrogenation.

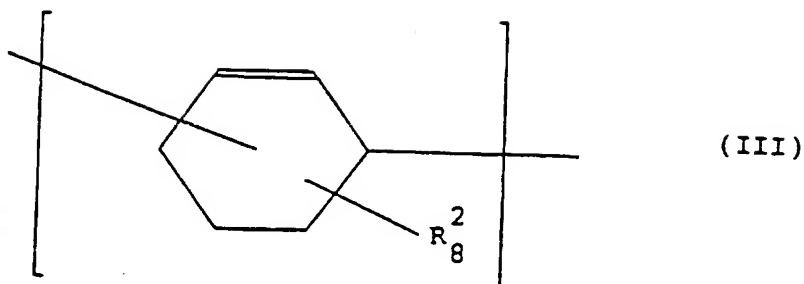
With respect to the cyclic conjugated diene monomer units which are contained as a part or all of the monomer units constituting the main chain of the cyclic conjugated diene polymer of the present invention, preferred examples thereof are those which are represented by the following formula (II), and most preferred examples thereof are those which are represented by the following formula (III):



wherein  $m$  is an integer of from 1 to 4, each  $R^1$  independently represents a hydrogen atom, a halogen atom, a  $C_1$ - $C_{20}$  alkyl group, a  $C_2$ -

C<sub>20</sub> unsaturated aliphatic hydrocarbon group,  
a C<sub>5</sub>-C<sub>20</sub> aryl group, a C<sub>3</sub>-C<sub>20</sub> cycloalkyl  
group, a C<sub>4</sub>-C<sub>20</sub> cyclodienyl group or a 5 to  
10-membered heterocyclic group having at  
least one nitrogen, oxygen or sulfur atom as  
a heteroatom, and each R<sup>2</sup> independently  
represents a hydrogen atom, a halogen atom, a  
C<sub>1</sub>-C<sub>20</sub> alkyl group, a C<sub>2</sub>-C<sub>20</sub> unsaturated  
aliphatic hydrocarbon group, a C<sub>5</sub>-C<sub>20</sub> aryl  
group, a C<sub>3</sub>-C<sub>20</sub> cycloalkyl group, a C<sub>4</sub>-C<sub>20</sub>  
cyclodienyl group or a 5 to 10-membered  
heterocyclic group having at least one nitro-  
gen, oxygen or sulfur atom as a heteroatom,  
or each R<sup>2</sup> independently represents a bond or  
a group such that two R<sup>2</sup> groups form a bridge  
represented by the formula  $-(CR_2^3)_n$  in which  
R<sup>3</sup> has the same meaning as defined for R<sup>1</sup> and  
n is an integer of from 1 to 10; and

5



wherein each  $R^2$  is as defined for formula (II).

10 In each of the above formulae (II) and (III), it is preferred that the alkyl group have 2 to 10 carbon atoms, the unsaturated aliphatic hydrocarbon group have 2 to 10 carbon atoms, the aryl group have 5 to 10 carbon atoms, the cycloalkyl group have 5 to 10 carbon atoms, the cyclodienyl group have 5 to 10 carbon atoms, and the heterocyclic group have a 5 to 8-membered ring structure.

Specific examples of substituents  $R^1$  and  $R^2$  include a methyl group, an ethyl group, an n-propyl group, an isopropyl group, an n-butyl group, a sec-butyl group, a tert-butyl group, a pentyl group, a hexyl group, a cyclopentyl group, a cyclohexyl group, a vinyl group, a phenyl group, a tolyl group, a naphthyl group, a cyclopentadienyl group, an indenyl group, a pyridyl group, and a piperidyl group.

In the present invention, for obtaining a cyclic conjugated diene block copolymer which has elastomeric properties (rubber elasticity), it is necessary that the block copolymer be comprised of at least two polymer blocks having a glass transition temperature ( $T_g$ ) higher than room temperature (agglomeration phases i.e., hard segments) and at least one polymer block having a  $T_g$  lower than room temperature (an elastomer phase, i.e., a soft segment), and that these two types of blocks form a microdomain structure.

In the polymeric molecular chain of such a block copolymer, the agglomeration phase functions as a physical crosslinking site at a temperature lower than  $T_g$ , so that the block copolymer has elastomeric properties.

On the other hand, at  $T_g$  or a temperature higher than  $T_g$ , the agglomeration phase becomes fluid, so that the block copolymer is imparted with flowability. Therefore, in this case, it becomes possible to perform a melt molding (such as injection molding, blow molding or injection molding) or a cast molding (such as cast film molding).

In the present invention, it is possible to cross-link the polymeric molecular chain of the cyclic conjugated diene copolymer, so as to impart the copolymer

with elastomeric properties (rubber elasticity).

Hereinbelow, the preferred embodiments of the cyclic conjugated diene block copolymer of the present invention are enumerated.

- 5 (1) A cyclic conjugated diene block copolymer, which has a glass transition temperature ( $T_g$ ) of 150 °C or more.
- (2) A cyclic conjugated diene block copolymer, wherein the block copolymer contains a polymer block  
10 having a glass transition temperature ( $T_g$ ) of 150 °C or more.
- (3) A cyclic conjugated diene block copolymer, which is an at least-tri-block copolymer.
- (4) A cyclic conjugated diene block copolymer, which  
15 is a block copolymer having a polymer block containing at least two A monomer units.
- (5) A cyclic conjugated diene block copolymer, which is a block copolymer having a polymer block consisting of at least two A monomer units.
- 20 (6) A cyclic conjugated diene block copolymer, which is an at least-di-block copolymer comprising at least one polymer block consisting of at least two A monomer units, and at least one polymer block consisting of monomer units of at least one type selected from the  
25 group of the B to the E monomer units.

- (7) A cyclic conjugated diene block copolymer, which is a diblock copolymer comprising one X polymer block containing at least one A monomer unit, and one Y polymer block comprised mainly of monomer units of at least one type selected from the B and the E monomer units, wherein the weight ratio of the X block to the Y block is from 1/99 to 99/1.
- (8) A cyclic conjugated diene block copolymer, which is an at least-tri-block copolymer comprising at least two X blocks each containing at least one A monomer unit, and at least one Y block comprised mainly of monomer units of at least one type selected from the B and the E monomer units, wherein the weight ratio of the at least two X blocks to the at least one Y block is from 1/99 to 99/1.
- (9) A cyclic conjugated diene block copolymer, which is a triblock copolymer comprising two X blocks containing at least one A monomer unit, and one Y block comprised mainly of monomer units of at least one type selected from the B and the E monomer units.
- (10) A cyclic conjugated diene block copolymer, which is an at least-tri-block copolymer, and wherein the at least-tri-block copolymer has a configuration represented by a formula selected from the group consisting of  $X - (Y - X)_p$ ,  $(X - Y)_q$ ,  $Y - (X - Y)_q$ ,  $[(Y -$

$X)_p\text{---}q$  ,  $[(X - Y)_p\text{---}q$  ,  $[(Y - X)_p\text{---}q$  , and  $[(X - Y)_p\text{---}q$  in which X and Y are as defined above, p is an integer of 1 or more, and q is an integer of 2 or more.

5 For obtaining a cyclic conjugated diene block copolymer having elastomeric properties (rubber elasticity), it is preferred that the cyclic conjugated diene block copolymer contain at least two X blocks [each X block being comprised mainly of at least one  
10 type of cyclic conjugated diene monomer unit and/or a monomer unit derived from the cyclic conjugated diene monomer unit (in an amount of at least 50 wt%, based on the total weight of the monomer units constituting the X block), or being comprised of at least one type of  
15 cyclic conjugated diene monomer unit and at least one type of vinyl aromatic monomer unit], and at least one Y block comprised mainly of at least one type of chain conjugated diene monomer unit and/or a monomer unit derived from the chain conjugated diene monomer unit  
20 (in an amount of at least 50 wt%, based on the total weight of the monomer units constituting the Y block). It is more preferred that the cyclic conjugated diene block copolymer contain at least two X blocks (each X block being comprised of at least one type of cyclic  
25 conjugated diene monomer unit and/or a monomer unit



derived from such a cyclic conjugated diene monomer unit), and at least one Y block comprised mainly of at least one type of chain conjugated diene monomer unit and/or a monomer unit derived from the chain conjugated diene monomer unit (in an amount of at least 50 wt%, based on the total weight of the monomer units constituting the Y block). It is especially preferred that the cyclic conjugated diene block copolymer be a polymer obtained by hydrogenation of a cyclic conjugated diene block copolymer containing at least two X blocks [each X block being comprised mainly of at least one type of cyclic conjugated diene monomer unit and/or a monomer unit derived from such a cyclic conjugated diene monomer unit (in an amount of at least 50 wt%, based on the total weight of the monomer units constituting the X block), or being comprised of at least one type of cyclic conjugated diene monomer unit and at least one type of vinyl aromatic monomer unit], and at least one Y block comprised mainly of at least one type of chain conjugated diene monomer unit and/or a monomer unit derived from the chain conjugated diene monomer unit (in an amount of at least 50 wt%, based on the total weight of the monomer units constituting the Y block). It is most preferred that the cyclic conjugated diene block copolymer be a polymer obtained by

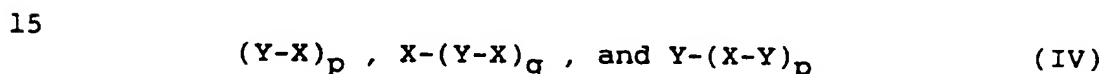
hydrogenation of a cyclic conjugated diene block copolymer containing at least two X blocks (each X block being comprised of at least one type of cyclic conjugated diene monomer unit and/or a monomer unit derived from the cyclic conjugated diene monomer unit), and at least one Y block comprised mainly of at least one type of chain conjugated diene monomer unit and/or a monomer unit derived from the chain conjugated diene monomer unit (in an amount of at least 50 wt%, based on the total weight of the monomer units constituting the Y block).

When the cyclic conjugated diene block copolymer of the present invention is used as an industrial material, it is preferred that the monomer units constituting the X block be monomer units derived from 1,3-cyclohexadiene, monomer units derived from 1,3-cyclohexadiene, and styrene, or monomer units derived from  $\alpha$ -methylstyrene, and that the monomer units constituting the Y block be monomer units derived from 1,3-butadiene and/or isoprene, which monomer units may be hydrogenated.

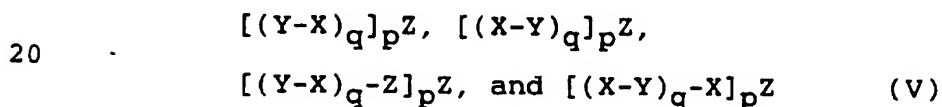
When the Y block is formed by polymerization of 1,3-butadiene monomer and/or isoprene monomer, the vinyl bond content of the monomers can be appropriately controlled without particular limitation. However,

for obtaining a cyclic conjugated diene block copolymer having excellent low temperature properties, the vinyl bond content is preferably within the range of from 10 to 90 mol%, more preferably from 20 to 80 mol%, based on the total number of moles of cis- and trans-1,4-bonds and the vinyl bond, which are present in the Y block.

In the present invention, for obtaining a block copolymer having elastomeric properties (rubber elasticity), for example, it is preferred that the block copolymer be linear block copolymers respectively represented by the formulae (IV) and radial block copolymers respectively represented by the formulae (V):



wherein  $p$  is an integer of 1 or more, and each  $q$  is an integer of 2 or more; and



wherein each  $p$  and each  $q$  are as defined above; and each  $Z$  independently represents a residue of a multifunctional coupling agent, such as dimethyldichlorosilane, methylene

chloride, silicon tetrachloride, tin tetrachloride or an epoxidized soybean oil, or a residue of a polymerization initiator, such as a multifunctional organometallic compound containing a metal belonging to Group IA of the Periodic Table.

Representative examples of cyclic conjugated diene block copolymers of the present invention, which have thermoplastic elastomer properties, include a cyclic conjugated diene block copolymer which is a triblock copolymer represented by the formula: X-Y-X, wherein the X block is present in an amount of from 10 to 60 wt%, preferably from 15 to 50 wt%, and the Y block is present in an amount of from 90 to 40 wt%, preferably from 85 to 50 wt%, and wherein the triblock copolymer has a number average molecular weight of from 1,000 to 200,000.

On the other hand, representative examples of cyclic conjugated diene block copolymers of the present invention, which can be employed as a tough plastic material, include a cyclic conjugated diene block copolymer which is a triblock copolymer represented by the formula: X-Y-X, wherein the X block is present in an amount of from 40 to 90 wt%, preferably from 45 to 85 wt%, and the Y block is present in an amount of from

60 to 10 wt%, preferably from 55 to 15 wt%, and wherein the triblock copolymer has a number average molecular weight of from 1,000 to 200,000.

5 In the present invention, the above-mentioned cyclic conjugated diene block copolymer having elastomeric properties may be a polymer that is subjected to at least one reaction selected from the group consisting of hydrogenation, halogenation, hydrohalogenation, alkylation, arylation, a ring-opening reaction and  
10 dehydrogenation.

Particularly, for obtaining a cyclic conjugated diene block copolymer which has excellent thermal properties, mechanical properties and chemical properties, it is preferred that the block copolymer be  
15 subjected to hydrogenation.

Hereinbelow, explanation is made with respect to a method for producing the improved cyclic conjugated diene polymer of the present invention. However, the production method is not limited to those which are  
20 described below.

For example, in the present invention, the cyclic conjugated diene polymer can be obtained using a stable catalyst comprising a mixture of a complex of at least one organometallic compound containing a metal belonging to Group IA of the Periodic Table with at least one  
25

complexing agent (first complexing agent), and at least one further complexing agent (second complexing agent).

The above-mentioned catalyst used in the present invention is thermally stable and does not cause disadvantageous side reactions, such as metalation, during the polymerization reaction.

By using such a catalyst for polymerization of at least one type of cyclic conjugated diene monomer, or for polymerization of at least one type of cyclic conjugated diene monomer and at least one comonomer copolymerizable with the cyclic conjugated diene monomer (selected from the class consisting of chain conjugated diene monomers, vinyl aromatic monomers, polar monomers, an ethylene monomer, and  $\alpha$ -olefin monomers), the cyclic conjugated diene polymer can be synthesized by anion polymerization, especially by living anion polymerization, from cyclic conjugated diene monomers under commercially advantageous temperature conditions, to thereby obtain a cyclic conjugated diene polymer having a narrow molecular weight distribution and a high 1,2-bond content in the main chain thereof and, thus, having excellent thermal properties.

Examples of metals belonging to Group IA of the Periodic Table (hereinafter, frequently simply referred to as "Group IA metals") which can be used in the present invention include lithium, sodium, potassium, rubidium, cesium and francium. Among these, lithium, sodium and potassium are preferred. Of these, lithium and sodium are especially preferred, and lithium is most preferred.

In the present invention, examples of organometallic compounds containing a Group IA metal include an organometallic compound containing lithium, sodium, potassium, rubidium, cesium or francium.

Among these, an organometallic compound containing lithium, sodium or potassium is preferred.

Of these, an organometallic compound containing lithium or sodium is especially preferred, and an organometallic compound containing lithium is most preferred.

Preferable examples of organometallic compounds to be used in the present invention include an organolithium compound, an organosodium compound and an organopotassium compound.

Among these, an organolithium compound and the organosodium compound are especially preferred, and an organolithium compound is most preferred.

The organolithium compound, which is preferably used in the present invention, is an organic compound having a structure such that at least one lithium atom is bonded to an organic molecule containing at least one carbon atom or an organic polymer having a structure such that at least one lithium atom is bonded to an organic polymer.

Examples of organic molecules include a  $C_1$ - $C_{20}$  alkyl group, a  $C_2$ - $C_{20}$  unsaturated aliphatic hydrocarbon group, a  $C_5$ - $C_{20}$  aryl group, a  $C_3$ - $C_{20}$  cycloalkyl group, a  $C_4$ - $C_{20}$  cyclodienyl group and the like.

Examples of organic polymers include polybutadiene, polyisoprene, polystyrene, poly- $\alpha$ -methylstyrene, polyethylene and the like.

Examples of organolithium compounds usable in the present invention include methyllithium, ethyllithium, n-propyllithium, isopropyllithium, n-butyllithium, sec-butyllithium, tert-butyllithium, pentyllithium, hexyllithium, allyllithium, cyclohexyllithium, phenyllithium, hexamethylenedilithium, cyclopentadienyllithium, indenyllithium, 9-fluorenyllithium, 9-anthrylmethyllithium, 1,1-diphenyl-n-hexyllithium, 1,1-diphenyl-3-methylpentyllithium, lithiumnaphthalene, butadienyldilithium, and isoprenyldilithium. Further, known oligomeric or polymeric organolithium compounds,



each containing a lithium atom in a polymeric molecular chain thereof, such as polybutadienyllithium, polybutadienyldilithium, polyisoprenyllithium, polyisoprenyldilithium, polystyryllithium, polystyryldilithium, and poly- $\alpha$ -methyl-dilithium can also be used.

There is no particular limitation with respect to the type of the organolithium compound, as long as a stable complex can be formed. Representative examples of such an organolithium compound include methyllithium, ethyllithium, n-propyllithium, iso-propyllithium, n-butyllithium, sec-butyllithium, tert-butyllithium, and cyclohexyllithium.

From the commercial point of view, preferable examples of organolithium compounds include n-butyllithium (n-BuLi), sec-butyllithium (s-BuLi), and tert-butyllithium (t-BuLi), and of these, n-butyllithium (n-BuLi) is most preferred.

In the present invention, each of the above-mentioned organometallic compounds containing a Group IA metal can be used individually or, if desired, in combination.

As mentioned above, the polymerization catalyst of the present invention is a mixture of a complex of at least one Group IA metal-containing organometallic compound with at least one first complexing agent, and

at least one second complexing agent. The first complexing agent and the second complexing agent may be the same or different.

There is no particular limitation with respect to the type of first complexing agent and the type of second complexing agent. However, it is preferred that the first complexing agent and the second complexing agent (each of which is hereinafter, frequently simply referred to as a "complexing agent") be independently an organic compound having an element which has a non-covalent electron pair capable of coordinating with a metal atom or metal ion in an organometallic compound containing the above-mentioned Group IA metal. Examples of such organic compounds include an organic compound containing at least one element selected from the group consisting of oxygen (O), nitrogen (N), sulfur (S) and phosphorus (P).

Preferred examples of such organic compounds include an ether, a metal alkoxide, an amine, and a thioether. Especially preferred examples of organic compounds include a cyclic ether, such as tetrahydrofuran, a crown ether or the like, a metal alkoxide, and an amine. Of these, an amine is most preferred.

Specifically, examples of such amines include an organic amine or an organic polymeric amine, which

contains at least one  $R^1R^2N$ - group (wherein each of  $R^1$  and  $R^2$  independently represents an alkyl group, an aryl group, or a hydrogen atom) which is a polar group having a non-covalent electron pair capable of coordinating with the organometallic compound containing a Group IA metal to thereby form a complex.

Among these amines, a tert-amine is especially preferred, and a tert-diamine is most preferred.

Specific examples of complexing agents usable in the present invention include diethyl ether, dibutyl ether, 1,2-dimethoxyethane, tetrahydrofuran, 2-methyltetrahydrofuran, tetrahydropyran, 18-crown-6, dibenzo-18-crown-6, 15-crown-5, dibenzo-24-crown-8, cryptand, lithium-t-butoxide, potassium-t-butoxide, di-t-butoxybarium, porphyrin, 1,2-dipiperazinoethane, trimethylamine, triethylamine, tri-n-butylamine, quinuclidine, pyridine, 2-methylpyridine, 2,6-dimethylpyridine, dimethylaniline, diethylaniline, tetramethyldiaminomethane, tetramethylethylenediamine, tetramethyl-1,3-propanediamine, tetramethyl-2-butene-1,4-diamine, tetramethyl-1,4-butanediamine, tetramethyl-1,6-hexanediamine, tetramethyl-1,4-phenylenediamine, tetramethyl-1,8-naphthalenediamine, tetramethylbenzidine, tetraethylethylenediamine, tetraethyl-1,3-propanediamine, tetramethyldiethylenetriamine, tetraethyldi-

ethylenetriamine, pentamethyldiethylenetriamine, pentaethyldiethylenetriamine, diazabicyclo[2.2.2]octane, 1,5-diazabicyclo[4.3.0]-5-nonene, 1,8-diazabicyclo[5.4.0]-7-undecene, 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane, tetrakis(dimethylamino)ethylene, tetraethyl-2-butene-1,4-diamine, (-)-2,3-dimethoxy-1,4-bis(dimethylamino)butane (DBB), (+)-1-(2-pyrrolidinylmethyl)pyrrolidine, 2,2'-bipyridyl, 4,4'-bipyridyl, 1,10-phenanthroline, hexamethylphosphoramide (HMPA), and hexamethylphosphoric triamide (HMPT).

Preferred examples of tert-amines usable in the present invention include trimethylamine, triethylamine, tri-n-butylamine, quinuclidine, pyridine, 2-methylpyridine, 2,6-dimethylpyridine, dimethylaniline, diethylaniline, tetramethyldiaminomethane (tetramethylmethylenediamine), tetramethylethylenediamine, tetramethyl-1,3-propanediamine (tetramethylpropylene diamine), tetramethyl-2-butene-1,4-diamine, tetramethyl-1,4-butanediamine (tetramethylbutylenediamine), tetramethyl-1,6-hexanediamine (tetramethylhexanediamine), tetramethyl-1,4-phenylenediamine, tetramethyl-1,8-naphthalenediamine, tetramethylbenzidine, tetraethylethylenediamine, tetraethyl-1,3-propanediamine, tetramethyldiethylenetriamine, tetraethyldiethylene-triamine, pentamethyldiethylenetriamine, pentaethyldi-

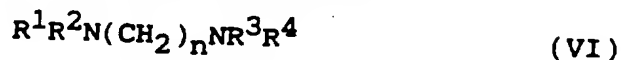
ethylenetriamine, 1,4-diazabicyclo[2.2.2]octane, 1,5-diazabicyclo[4.3.0]-5-nonene, 1,8-diazabicyclo[5.4.0]-7-undecene, 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane, tetrakis(dimethylamino)ethylene, tetraethyl-2-butene-1,4-diamine, (-)-2,3-dimethoxy-1,4-bis(dimethylamino)butane (DDB), (+)-1-(2-pyrrolidinylmethyl)pyrrolidine, 2,2'-bipyridyl, 4,4'-bipyridyl, 1,10-phenanthroline, hexamethylphosphoramide (HMPA), and hexamethylphosphoric triamide (HMPT).

10        Especially preferred examples of complexing agents usable in the present invention include aliphatic amines, and of these, an aliphatic diamine is most preferred.

15        Most preferred examples of aliphatic diamines include tetramethylmethylenediamine (TMMDA), tetraethylmethylenediamine (TEMDA), tetramethylethylenediamine (TMEDA), tetraethylethylenediamine (TEEDA), tetramethylpropylenediamine (TMPDA), tetraethylpropylenediamine (TEPDA), tetramethylbutylenediamine (TMBDA), tetraethylbutylenediamine (TEBDA), tetramethylpentanediamine, tetraethylpentanediamine, tetramethylhexanediamine (TMHDA), tetraethylhexanediamine (TEHDA), and 1,4-diazabicyclo[2.2.2]octane (DABCO).

25        From the commercial point of view, it is most preferred to use an aliphatic diamine represented by

formula (VI) shown below, which forms a stable complex with an organolithium compound:



5 wherein each of  $R^1$ ,  $R^2$ ,  $R^3$  and  $R^4$  independently represents a  $C_1$ - $C_{20}$  alkyl group, and  $n$  represents an integer of from 1 to 20.

10 It is preferred that such an aliphatic diamine be a diamine having, between two nitrogen atoms thereof, 1 to 6 carbon atoms, preferably 1 to 3 carbon atoms, most preferably 2 carbon atoms.

15 Especially preferred examples of complexing agents usable in the present invention include tetramethylethylenediamine (TMEDA) and 1,4-diazabicyclo-[2.2.2]octane (DABCO). Of these, tetramethylethylenediamine (TMEDA) is most preferred.

The above-mentioned complexing agents, preferably amines, may be used individually or, if desired, in combination.

20 From the commercial point of view, it is preferred that the catalyst to be used in the present invention be one which is prepared from an organometallic compound (especially an organolithium compound), containing at least one Group IA metal, selected from the group consisting of methyllithium (MeLi), ethyllithium (EtLi), n-propyllithium (n-PrLi), iso-propyllithium

25

(i-PrLi), n-butyllithium (n-BuLi), sec-butyllithium (s-BuLi), tert-butyllithium (t-BuLi), and cyclohexyllithium, and at least one complexing agent (especially an amine) selected from the group consisting of tetramethylmethylenediamine (TMMDA), tetramethylethylenediamine (TMEDA), tetramethylpropylenediamine (TMPDA), tetramethylhexanediamine (TMHDA), and 1,4-diazabicyclo[2.2.2]octane (DABCO).

In the present invention, it is most preferred that the catalyst be one which is prepared from an organolithium compound selected from the group consisting of n-butyllithium (n-BuLi), sec-butyllithium (s-BuLi), and tert-butyllithium (t-BuLi), and at least one amine selected from the group consisting of tetramethylethylenediamine (TMEDA) and 1,4-diazabicyclo[2.2.2]octane (DABCO).

In the present invention, there is no particular limitation with respect to the method of synthesizing a complex of at least one organometallic compound containing a Group IA metal with at least one first complexing agent. The synthesis can be conducted by conventional techniques.

Examples of such conventional techniques include a method comprising dissolving the organometallic compound containing a Group IA metal in an organic solvent

in an atmosphere of a dried inert gas, and adding thereto a solution of the first complexing agent, and a method comprising dissolving the first complexing agent in an organic solvent in an atmosphere of a dried inert gas, and adding thereto a solution of the organometallic compound containing a Group IA metal. Of these methods, a preferable method can be appropriately selected.

With respect to the above-mentioned organic solvent, it is preferred that an organic solvent to be used be appropriately selected depending on the type and amount of the organometallic compound and the type and amount of the first complexing agent, and be well deaerated and dried prior to use.

Further, it is preferred that the reaction for obtaining the complex of at least one organometallic compound with at least one first complexing agent be conducted at  $-100$  to  $100$  °C. From the commercial point of view, it is preferred that the reaction for obtaining the complex be conducted at from room temperature to  $80$  °C, more preferably from room temperature to  $60$  °C.

Examples of inert gases include helium, nitrogen and argon. Of these, from the commercial point of view, nitrogen and argon are preferred.



In the present invention, the above-mentioned complex is formed by reacting at least one Group IA metal-containing organometallic compound with at least one first complexing agent.

5           Further, in the present invention, it is preferred that the Group IA metal in the complex be present in the form of an association of 2 to 10 metal atoms, more preferably 2 to 8 metal atoms, most preferably 2 to 6 metal atoms.

10           In the preparation of the above-mentioned complex of at least one Group IA metal-containing organometallic compound with at least one first complexing agent, it is preferred to employ the following molar ratio of the Group IA metal contained in the organometallic  
15           compound relative to the complexing agent. The molar ratio is:

generally,

$$A_1/B_1 = 200/1 \text{ to } 1/100,$$

preferably,

20            $A_1/B_1 = 100/1 \text{ to } 1/80,$

more preferably,

$$A_1/B_1 = 80/1 \text{ to } 1/50,$$

still more preferably,

$$A_1/B_1 = 50/1 \text{ to } 1/20,$$

25           further more preferably,

$A_1/B_1 = 20/1$  to  $1/10$ ,  
most preferably,

$A_1/B_1 = 1/0.2$  to  $1/1.2$

5 wherein  $A_1$  is the molar amount of the Group  
IA metal contained in the organometallic  
compound, and  $B_1$  is the molar amount of the  
first complexing agent.

As specific examples of the polymerization method  
of the present invention, in which a polymerization is  
10 conducted in the presence of a catalyst comprising a  
mixture of the complex of at least one Group-IA metal-  
containing organometallic compound and at least one  
first complexing agent, and at least one second com-  
plexing agent, the following methods can be mentioned:  
15 (1) a method comprising adding the second complexing  
agent to a polymerization solvent, and adding thereto  
the complex of the Group IA metal-containing organome-  
tallic compound with the first complexing agent to form  
a catalyst, followed by a polymerization in the presence  
20 of the catalyst;  
(2) a method comprising adding the complex of the Group  
IA metal-containing organometallic compound with the  
first complexing agent to a polymerization solvent, and  
adding thereto the second complexing agent to form a  
25 catalyst, followed by a polymerization reaction in the

presence of a catalyst;

- (3) a method comprising forming the complex of the Group IA metal-containing organometallic compound with the first complexing agent in a polymerization solvent, and adding in situ thereto the second complexing agent to form a catalyst, followed by polymerization in the presence of the catalyst; and
- (4) a method comprising forming the complex of the Group IA-metal containing organometallic compound with the first complexing agent using the first complexing agent in such a large amount that some of the first complexing agent added remains unreacted without forming a complex, followed by polymerization in the presence of the complex and the unreacted first complexing agent, wherein the unreacted first complexing agent functions as the second complexing agent.

Of these methods, a preferable method can be appropriately selected. However, when the polymerization reaction is conducted at high temperatures, especially at a temperature of 60 °C or higher, it is preferred that the catalyst is provided by a method comprising the steps of forming the complex, and subsequently mixing the complex with the second complexing agent, as in the case of methods (1) to (3) above.

Further, with respect to the amount of the second

complexing agent to be copresent with the complex in the form of a mixture thereof, there is no particular limitation. However, in the present invention, it is preferred that, at the time of initiation of a polymerization reaction of a cyclic conjugated diene monomer, the at least one organometallic compound, the at least one first complexing agent, and the at least one second complexing agent be present in the following molar relationships.

The molar ratio is:

generally,

$$A_3/B_3 = 100/1 \text{ to } 1/200,$$

preferably,

$$A_3/B_3 = 80/1 \text{ to } 1/100,$$

more preferably,

$$A_3/B_3 = 50/1 \text{ to } 1/80,$$

still more preferably,

$$A_3/B_3 = 20/1 \text{ to } 1/50,$$

most preferably,

$$A_3/B_3 = 10/1 \text{ to } 1/20,$$

wherein  $A_3$  is the molar amount of the Group IA metal contained in the organometallic compound, and  $B_3$  is the molar amount of the total of the first complexing agent and the second complexing agent.

In the method of the present invention, especially for obtaining a cyclic conjugated diene polymer which has a high content of A monomer units having 1,2-bonds and therefore has excellent thermal properties, the molar ratio is:

preferably,

$$A_3/B_3 = 2/1 \text{ to } 1/10;$$

most preferably (from the commercial point of view),

$$A_3/B_3 = 1.25/1 \text{ to } 1/5,$$

wherein  $A_3$  and  $B_3$  are as defined above.

In a most preferred embodiment of the method of the present invention, a complex is formed which comprises at least one organometallic compound containing a Group IA metal, and at least one first complexing agent and then, the complex is mixed with at least one second complexing agent to thereby form a catalyst having the following molar ratio, followed by polymerization in the presence of the catalyst:

$$A_2/B_2 = 1/0.25 \text{ to } 1/1,$$

wherein  $A_2$  is the molar amount of the Group IA metal contained in the organometallic compound contained in the complex, and  $B_2$  is the molar amount of the first complexing agent contained in the complex.

Representative examples of polymerization methods of the present invention include a method comprising forming a complex having the following molar ratio of the Group IA metal-containing organometallic compound and the first complexing agent by reacting  $A_2$  mol of an organolithium compound selected from the group consisting of n-butyllithium (n-BuLi), sec-butyllithium (s-BuLi), and tert-butyllithium (t-BuLi), with  $B_2$  mol of at least one amine selected from the group consisting of tetramethylethylenediamine (TMEDA) and 1,4-diazabicyclo[2.2.2]octane (DABCO), wherein the molar ratio is:

$$A_2/B_2 = 1/0.25 - 1/1,$$

wherein  $A_2$  and  $B_2$  are as defined above; and performing the polymerization reaction under conditions, wherein the above complex and the second complexing agent are copresent in amount relationships as defined above for  $A_3/B_3$ .

In the present invention, for example, a preferred form of the complex has a structure which can be represented, for example, by the following formula (VII):



wherein G represents at least one type of organometallic compound containing a Group IA

metal; J represents at least one type of the first complexing agent; and each of g, j and k is an integer of 1 or more.

The complex obtained by any of the above-mentioned  
5 methods is thermally unstable. However, in the catalyst used in the present invention, which comprises a mixture of the complex and the second complexing agent, the thermally unstable complex is stabilized by the second complexing agent which is copresent with the  
10 complex. Therefore, by the use of such a catalyst, it has become possible to perform a living anionic polymerization of the cyclic conjugated diene monomer even under relatively high temperature conditions, such as room temperature or more, especially 60 °C or more.  
15 Furthermore, by the use of such a catalyst, it has become possible to produce a cyclic conjugated diene polymer having a narrow molecular weight distribution even under relatively high temperature conditions, such as room temperature or more.  
20 Further, in the method of the present invention, even when a large amount of the complexing agent is present in the polymerization system, unfavorable side reactions, such as metalation, are not likely to occur, so that it is possible to produce a cyclic conjugated  
25 diene polymer in which cyclic conjugated diene monomer

units having 1,2-bonds are introduced in a relatively high ratio.

5 With respect to the type of the second complexing agent to be used with the complex, there is no particular limitation, and the type of the first complexing agent and the type of the second complexing agent may be the same or different. However, from the economical point of view, it is preferred that the type of the first complexing agent and the type of the second  
10 complexing agent be the same.

With respect to the method for polymerization, there is no particular limitation. An appropriate polymerization method can be selected. Examples of polymerization methods include a gaseous phase polymer-  
15 ization, a bulk polymerization and a solution polymerization.

The polymerization reactions can be conducted in various manners, such as a batchwise, a semi-batchwise or a continuous manner.

20 The reactor for conducting the polymerization can also be appropriately selected according to the properties of the polymer to be obtained, the reaction conditions and the like. Examples of reactors include an autoclave, a coil reactor, a tube reactor, a kneader,  
25 and an extruder.



When the polymerization method of the present invention is conducted by solution polymerization, suitable examples of polymerization solvents to be used include aliphatic hydrocarbons, such as butane, n-pentane, n-hexane, n-heptane, n-octane, iso-octane, n-nonane and n-decane; alicyclic hydrocarbons, such as cyclopentane, methylcyclopentane, cyclohexane, methylcyclohexane, ethylcyclohexane, cycloheptane, cyclooctane, decalin, and norbornane; aromatic hydrocarbons, such as benzene, toluene, xylene, ethylbenzene, and cumene; and ethers, such as diethyl ether, tetrahydrofuran, and tetrahydropyran. An appropriate solvent can be selected according to the properties of the polymer to be obtained, the reaction conditions and the like.

These polymerization solvents may be used individually or, if desired, in combination.

Preferred examples of polymerization solvents include aliphatic hydrocarbons, alicyclic hydrocarbons, and aromatic hydrocarbons.

Most preferred polymerization solvents are aliphatic hydrocarbons, alicyclic hydrocarbons, and a combination of these solvents.

Specific examples of most preferred polymerization solvents in the present invention are at least one polymerization solvent selected from n-hexane, cyclo-

hexane and methylcyclohexane.

In the polymerization method of the present invention, the amount of the polymerization catalyst is not specifically limited, and may vary depending on the intended use of the polymer to be produced. However, the polymerization catalyst is generally used in an amount of from  $1 \times 10^{-6}$  mol to  $5 \times 10^{-1}$  mol, preferably from  $5 \times 10^{-6}$  mol to  $1 \times 10^{-1}$  mol, in terms of the molar amount of metal atom per mol of the monomer or monomers.

In the polymerization method of the present invention, the polymerization reaction temperature may vary according to the other polymerization reaction conditions. However, the polymerization reaction temperature is generally from  $-100$  to  $150$  °C, preferably from  $-80$  to  $120$  °C, more preferably from  $-30$  to  $110$  °C, and most preferably from  $0$  to  $100$  °C.

Further, from a commercial point of view, it is advantageous that the polymerization reaction temperature be from room temperature to  $90$  °C, more preferably from  $30$  to  $85$  °C, and most preferably from  $40$  to  $80$  °C.

In the polymerization method of the present invention, the polymerization reaction time is not specifically limited, and the polymerization reaction time may vary depending on the intended use of the polymer and

the other polymerization reaction conditions. However, from a commercial point of view, the polymerization reaction time is generally not longer than 48 hours, more preferably for 0.5 to 24 hours, and most preferably for 1 to 10 hours.

Further, it is preferred that the polymerization reaction be conducted in an atmosphere of an inert gas, such as helium, nitrogen or argon. It is especially preferred to use a highly purified, well dried inert gas containing impurities, such as oxygen and carbon dioxide, in an amount as small as possible.

From a commercial point of view, it is preferred to use highly purified, well dried nitrogen or argon, and it is most preferred to use highly purified and well-dried nitrogen.

With respect to the pressure in the polymerization reaction system, there is no particular limitation, and a widely varied pressure can be chosen as long as the pressure is sufficient to maintain the monomer or monomers and the solvent at a liquid state at a polymerization temperature within the above-mentioned range.

Further, it is preferred that care be taken to prevent the intrusion of impurities, which deactivate a polymerization catalyst or growing (active) of the

terminals of the polymer being formed, such as water, oxygen and carbon dioxide, into the polymerization reaction system.

5 In the method of the present invention, for separating and recovering the cyclic conjugated diene polymer from a polymer solution, a conventional technique can be used which is generally used for recovering a conventional polymer from a polymer solution (polymerization reaction mixture).

10 Examples of such conventional methods include a steam-coagulation method comprising directly contacting a polymerization reaction mixture with steam; a precipitation method comprising adding a poor solvent for a polymer to a polymerization reaction mixture, thereby precipitating the polymer; a method comprising heating a polymerization reaction mixture in a polymerization reactor, thereby distilling off the solvent; a method comprising contacting a polymerization reaction mixture with a heating roll, thereby distilling off the solvent; a method comprising extruding a polymerization reaction mixture using an extruder having a vent, while distilling off a solvent through the vent, thereby obtaining a pelletized polymer; and a method comprising placing a polymerization reaction mixture into hot water and, then, extruding the resultant mixture using

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an extruder having a vent, while distilling off a solvent and water through the vent, thereby obtaining a pelletized polymer. A most appropriate method can be selected depending on the properties of the cyclic conjugated diene polymer to be obtained and the solvent used.

With respect to the method of the present invention, the polymerization reaction may optionally be followed by at least one reaction selected from hydrogenation, halogenation, hydrohalogenation, alkylation, arylation, a ring-opening reaction and dehydrogenation.

The above-mentioned optional reactions can be performed in the absence or presence of a conventional catalyst.

For example, when the method of the present invention comprises the two steps of the polymerization reaction and a subsequent hydrogenation reaction, the polymerization reaction is first performed to synthesize a polymer containing cyclic conjugated diene monomer units in the main chain of the polymer, and subsequently, a hydrogenation reaction of the obtained polymer is performed in the presence of a hydrogenation catalyst to hydrogenate a part or all of the

carbon-to-carbon double bonds in the polymer, thereby obtaining a hydrogenated cyclic conjugated diene polymer.

5           A specific example of methods for producing a hydrogenated cyclic conjugated diene polymer is as follows. A polymerization reaction for obtaining a polymer comprising or consisting essentially of cyclic conjugated diene monomer units is conducted, and after  
10   a predetermined (intended) polymerization degree has been reached, the polymerization reaction is terminated. Then, a hydrogenation catalyst is added to a reactor containing the obtained cyclic conjugated diene polymer, and hydrogen gas is introduced to the reactor  
15   thereby effecting a hydrogenation reaction of the polymer to thereby obtain a hydrogenated cyclic conjugated diene polymer.

          More specifically, there can be mentioned a method in which the polymerization reaction is terminated by a  
20   conventional method, and then a hydrogenation catalyst is added to and hydrogen gas is introduced to the same reactor as used in the polymerization reaction, thereby producing a hydrogenated polymer in a batchwise manner.

          There can also be mentioned a method in which the  
25   polymerization reaction is terminated by a conventional

method, the reaction mixture is transferred to another reactor, and a hydrogenation catalyst is added to and hydrogen gas is introduced to the reactor containing the reaction mixture, thereby producing a hydrogenated polymer in a semi-batchwise manner.

Further, a hydrogenated polymer may be produced in a continuous manner by performing the polymerization reaction and hydrogenation reaction continuously in a tube type reactor.

An appropriate method can be selected from these methods according to the objective and needs.

When the method of the present invention includes a hydrogenation reaction, the hydrogenation reaction is performed in an atmosphere of hydrogen, preferably in the presence of a hydrogenation catalyst.

In the present invention, the hydrogenation reaction is generally conducted by a method in which a polymer solution is maintained at a predetermined temperature in an atmosphere of hydrogen gas or an inert gas, and a hydrogenation catalyst is added to the polymer solution while agitating or not agitating. After maintaining the solution at the temperature of reaction, hydrogen gas is introduced into the reaction system until a predetermined level of pressure is reached.

The hydrogenation reaction can be conducted in a conventional manner, namely, in a batchwise, a semi-batchwise or a continuous manner. These manners can be employed individually or in combination.

5        The type and amount of the hydrogenation catalyst to be used in the present invention are not particularly limited as long as the catalyst used can provide a desired degree of hydrogenation. However, practically, the hydrogenation catalyst to be used in the present  
10       invention can be selected from a homogeneous catalyst (e.g., an organometallic compound, an organometallic complex) and a heterogeneous catalyst (e.g., a solid catalyst, a catalyst supported by a carrier) each of which contains at least one member selected from the  
15       group consisting of metals belonging to Groups IV A to VIII of the Periodic Table and rare earth metals.

A most preferred hydrogenation catalyst in the present invention is a homogeneous hydrogenation catalyst, i.e., an organometallic compound or complex which  
20       contains at least one member selected from the group consisting of Group IV A to VIII metals and rare earth metals, or a carrier-supported catalyst containing a Group VIII metal (a solid catalyst).

These organometallic compounds or complexes as  
25       homogeneous hydrogenation catalysts can be supported by



an inorganic or organic compound, such as silica, a zeolite or a crosslinked polystyrene.

Especially preferred examples of metals contained in the hydrogenation catalyst to be used in the present invention include titanium, cobalt, nickel, ruthenium, rhodium, and palladium.

When the above-mentioned metals are contained in a homogeneous hydrogenation catalyst, it is requisite that a ligand such as hydrogen, a halogen, a nitrogen compound or an organic compound, be coordinated with or bonded to such metals. These ligands can be used individually or in combination. When these ligands are used in combination, it is especially preferred that an appropriate combination of ligands be selected so that the resultant organometallic compound or complex becomes soluble in the solvent used.

Various types of hydrogenation catalysts can be used individually or, if desired, in combination.

Further, from a commercial point of view, it is most preferred that, as a hydrogenation catalyst, use is made of a combination of an organometallic compound or complex which contains at least one member selected from the group consisting of Group IV A to VIII metals and rare earth metals, and at least one organometallic compound containing a metal selected from the group

consisting of Group IA to IIA metals and Group IIIB metals, such as alkyllithium, alkylmagnesium, and alkylaluminum.

5 When the hydrogenation catalyst is a solid catalyst, the above-mentioned metals can be used as they are. However, generally, it is preferred that the metals to be used as a catalyst are in a state in which they are supported by a carrier such as carbon, alumina, silica or barium sulfate.

10 Preferred examples of solid catalysts include carrier-supported catalysts containing at least one metal selected from rhenium, iron, cobalt, nickel, ruthenium, rhodium, palladium and platinum. Especially preferred examples of solid catalysts include carrier-  
15 supported catalysts containing at least one metal selected from ruthenium, rhodium and palladium.

These catalysts can be used individually or in combination.

20 When the cyclic conjugated diene polymer obtained by the method of the present invention is a hydrogenated polymer, the amount of hydrogenation catalyst to be used for a hydrogenation reaction can be appropriately determined depending on the type (e.g., the structure of the main chain and molecular weight) of the polymer  
25 to be hydrogenated, or the hydrogenation reaction condi-

tions (e.g., solvent, temperature, concentration, and viscosity of the solution). However, the amount of the hydrogenation catalyst is generally within the range of from 0.1 to 100,000 ppm, preferably from 1 to 50,000 ppm, more preferably from 5 to 10,000 ppm, and most preferably from 10 to 10,000 ppm, in terms of the concentration of metal atoms, based on the amount of the polymer to be hydrogenated.

When the amount of the hydrogenation catalyst is extremely small, a satisfactory rate of hydrogenation reaction cannot be obtained. When the amount of the hydrogenation catalyst is too large, the rate of hydrogenation reaction becomes high, but the use of too large an amount of the hydrogenation catalyst is disadvantageous from an economical point of view. In addition, when the amount of the hydrogenation catalyst is too large, the separation and recovery of the hydrogenation catalyst become difficult, leading to undesirable results, for example, adverse effects of the residual catalyst on the polymer.

In the method of the present invention, it is preferred that a solvent to be used for the hydrogenation reaction be inert to the hydrogenation catalyst and capable of well dissolving therein the polymer to be hydrogenated.

From a commercial point of view, it is preferred to choose solvents to be used for the hydrogenation reaction from aliphatic hydrocarbons, alicyclic hydrocarbons, and aromatic hydrocarbons. Most preferred solvents are aliphatic hydrocarbons, alicyclic hydrocarbons, and a mixture of these solvents.

In the present invention, from a commercial point of view, it is advantageous that the polymerization reaction and the hydrogenation reaction be consecutively conducted. Therefore, it is preferred that the solvent to be used for the hydrogenation reaction be the same as the solvent used for the polymerization reaction.

In the present invention, there is no particular limitation with respect to the concentration of a polymer solution to be subjected to the hydrogenation reaction. However, the polymer concentration of the polymer solution is preferably from 1 to 90 wt%, more preferably from 2 to 60 wt%, most preferably from 3 to 40 wt%.

When the polymer concentration of the polymer solution is lower than the above-mentioned range, the operation for the hydrogenation reaction becomes inefficient and disadvantageous from an economic point of view. On the other hand, when the concentration of the

polymer solution is higher than the above-mentioned range, the viscosity of the polymer solution becomes high, leading to a lowering of the reaction rate.

5 In the present invention, the reaction temperature for hydrogenation can be appropriately selected, but is generally from -78 to 500 °C, preferably from -10 to 300 °C, and more preferably from 20 to 250 °C.

10 When the reaction temperature is lower than the above-mentioned range, a satisfactorily high reaction rate cannot be achieved. On the other hand, when the reaction temperature is higher than the above-mentioned range, disadvantages are likely to be caused such that not only is the hydrogenation catalyst deactivated, but also the polymer is deteriorated.

15 The pressure of the hydrogenation reaction system is generally from 0.1 to 500 kg/cm<sup>2</sup>G, preferably from 1 to 400 kg/cm<sup>2</sup>G, more preferably from 2 to 300 kg/cm<sup>2</sup>G.

20 When the pressure of the hydrogenation reaction system is lower than the above-mentioned range, a satisfactorily high reaction rate cannot be achieved. When the pressure is higher than the above-mentioned range, the reaction rate becomes high, but an expensive pressure-resistant reaction apparatus is required, which is economically disadvantageous. Further, such a  
25 high pressure may cause a hydrocracking of the polymer

during the hydrogenation reaction.

The reaction time for hydrogenation is not particularly limited, and may vary depending on the type and amount of the hydrogenation catalyst, the concentration of the polymer solution, and the temperature and pressure of the reaction system. However, the reaction time for hydrogenation is generally from 5 minutes to 240 hours, preferably from 10 minutes to 100 hours, and more preferably from 30 minutes to 48 hours.

If desired, after completion of the hydrogenation reaction, the hydrogenation catalyst can be recovered from the resultant hydrogenation reaction mixture by a conventional method, such as adsorption-separation of the catalyst by means of an adsorbent, sedimentation separation, filtration separation, or removal of the catalyst by washing with water or a lower alcohol in the presence of an organic acid and/or an inorganic acid.

The separation and recovery of the hydrogenated cyclic conjugated diene polymer of the present invention from the hydrogenation reaction mixture can be conducted by a conventional method which is generally used for recovering a conventional polymer from a polymerization reaction mixture.

Examples of such conventional methods include a

steam-coagulation method comprising directly contacting a polymerization reaction mixture with steam; a precipitation method comprising adding a poor solvent for a polymer to a polymerization reaction mixture, thereby precipitating the polymer; a method comprising heating a polymerization reaction mixture in a polymerization reactor, thereby distilling off the solvent; a method comprising contacting a polymerization reaction mixture with a heating roll, thereby distilling off the solvent; a method comprising extruding a polymerization reaction mixture using an extruder having a vent, while distilling off a solvent through the vent, thereby obtaining a pelletized polymer; and a method comprising placing a polymerization reaction mixture into hot water and, then, extruding the resultant mixture using an extruder having a vent, while distilling off a solvent and water through the vent, thereby obtaining a pelletized polymer. A most appropriate method can be selected depending on the properties of the cyclic conjugated diene polymer to be obtained and the solvent used.

By hydrogenating A monomer units of the cyclic conjugated diene polymer of the present invention which has a high content of A monomer units having 1,2-bonds, a polymer which is a commercially most preferable

material having especially excellent thermal and mechanical properties can be obtained.

As mentioned above, in the method of the present invention, if desired, the polymerization reaction may  
5 be followed by at least one reaction selected from hydrogenation, halogenation, hydrohalogenation, alkylation, arylation, ring-opening reactions and dehydrogenation.

In the method of the present invention, the dehydrogenation reaction can be performed by employing a  
10 conventional technique.

More specifically, the cyclic conjugated diene polymer of the present invention is produced by the polymerization method of the present invention, and  
15 consecutively or after separating and recovering the cyclic conjugated diene polymer from the reaction mixture, a part or all of A monomer units contained in the polymer are converted to aromatic rings.

With respect to the dehydrogenation reaction in  
20 the present invention, there is no particular limitation and a conventional method for dehydrogenation can be employed. However, it is preferred that a part or all of A monomer units in the polymer main chain be converted to aromatic rings, more preferably to benzene  
25 rings.



The dehydrogenation reaction in the present invention may be either a catalytic reaction or a stoichiometric reaction. Generally, the dehydrogenation reaction is conducted as follows. The cyclic conjugated diene polymer is used as it is or, if desired, the polymer is diluted with a solvent, preferably an organic solvent. If desired, a dehydrogenation catalyst or a dehydrogenation reagent is added to the polymer. Subsequently, the dehydrogenation reaction is conducted under predetermined conditions.

With respect to the type of the dehydrogenation reaction in the present invention, a conventional type of dehydrogenation reaction can be employed according to the needs. Examples of conventional types of dehydrogenation reactions include a reaction by a method comprising pulling out a hydrogen atom or a hydrogen molecule directly from a monomer unit in the polymer main chain; a reaction by a method comprising pulling out hydrogen in a state in which it is contained in a compound, such as sulfonated hydrogen and hydrogen halogenide; and a reaction by a method comprising pulling out hydrogen by a disproportionation reaction.

As an example of a simple and easy method for the dehydrogenation reaction using a generally available reagent, a method employing a quinone as a dehydrogena-

tion reagent can be mentioned.

Representative examples of quinones include 1,4-benzoquinone (quinone), tetrachloro-1,2-benzoquinone (o-chloranil), tetrachloro-1,4-benzoquinone (p-chloranil), tetrabromo-1,2-benzoquinone (o-bromanil), tetrabromo-1,4-benzoquinone (p-bromanil), tetrafluoro-1,2-benzoquinone, tetrafluoro-1,4-benzoquinone, tetraiodo-1,2-benzoquinone, tetraiodo-1,4-benzoquinone, tetrahydroxy-1,4-benzoquinone, 2,3-dichloro-5,6-dicyano-p-benzoquinone, 1,2-naphthoquinone, 1,4-naphthoquinone, anthraquinone, 1-chloroanthraquinone, 1-bromoanthraquinone, 1-fluoroanthraquinone, 1-iodoanthraquinone, 2,6-dihydroxyanthraquinone, 1,5-dihydroxyanthraquinone, 1,4,4a,9a-tetrahydroanthraquinone, and phenanthrenequinone.

From a commercial point of view, preferred examples of quinones as a dehydrogenation reagent are 1,4-benzoquinone (quinone), tetrachloro-1,2-benzoquinone (o-chloranil), tetrachloro-1,4-benzoquinone (p-chloranil), tetrabromo-1,2-benzoquinone (o-bromanil), and tetrabromo-1,4-benzoquinone (p-bromanil). Of these, tetrachloro-1,4-benzoquinone (p-chloranil) is most preferred.

When the dehydrogenation reaction in the present invention is performed by dissolving the cyclic conju-

gated diene polymer in an organic solvent, the type and amount of the organic solvent are not particularly limited as long as the solvent used can satisfactorily dissolve the cyclic conjugated diene polymer. The organic solvent can be appropriately selected depending on the solubility of the cyclic conjugated diene polymer.

Examples of organic solvents to be used in the dehydrogenation reaction include aliphatic hydrocarbons, such as butane, n-pentane, n-hexane, n-heptane, n-octane, iso-octane, n-nonane, and d-decane; alicyclic hydrocarbons, such as cyclopentane, methylcyclopentane, cyclohexane, methylcyclohexane, ethylcyclohexane, cycloheptane, cyclooctane, decalin, and norbornane; aromatic hydrocarbons, such as benzene, toluene, xylene, ethylbenzene and cumene; ethers, such as diethyl ether, tetrahydrofuran and tetrahydropyran; and hydrocarbon halogenides, such as chloroform, methylene chloride, chlorobenzene, dichlorobenzene, and trichlorobenzene.

With respect to the dehydrogenation reaction temperature, the temperature may vary according to the other reaction conditions. However, the dehydrogenation reaction temperature is generally from 0 to 350 °C, preferably from 0 to 300 °C, more preferably

from 0 to 250 °C, and most preferably from 0 to 200 °C. Further, from a commercial point of view, it is advantageous to perform the dehydrogenation reaction at a temperature in the range of from room temperature to 200 °C.

The dehydrogenation reaction time is not specifically limited, and the dehydrogenation reaction time may vary depending on the intended use of the dehydrogenated polymer and the other dehydrogenation reaction conditions. However, the dehydrogenation reaction time is generally not longer than 48 hours, preferably from 1 to 24 hours.

Further, it is preferred that the dehydrogenation reaction be conducted in an atmosphere of an inert gas, such as nitrogen, argon or helium. For inhibiting side reactions, it is especially preferred that such an inert gas be a highly purified, well dried inert gas.

With respect to the pressure in the dehydrogenation reaction system, there is no particular limitation, and a widely varied pressure can be chosen as long as the pressure is sufficient to maintain the catalyst, reagent and solvent at a liquid state at a dehydrogenation temperature within the above-mentioned range.

Further, it is preferred that care be taken to

prevent the intrusion of impurities, which deactivate a dehydrogenation catalyst and a dehydrogenation reagent or cause a cross-linking, a degradation or the like of the cyclic conjugated diene polymer, such as water, oxygen and carbon dioxide, into the dehydrogenation reaction system.

After completion of the dehydrogenation reaction, the separation and recovery of the polymer of the present invention from the dehydrogenation reaction mixture can be conducted by a conventional method which is generally used for recovering a conventional polymer from a polymerization reaction mixture.

Examples of such conventional methods include a steam-coagulation method comprising directly contacting a polymerization reaction mixture with steam; a precipitation method comprising adding a poor solvent for a polymer to a polymerization reaction mixture, thereby precipitating the polymer; a method comprising heating a polymerization reaction mixture in a polymerization reactor, thereby distilling off the solvent; a method comprising contacting a polymerization reaction mixture with a heating roll, thereby distilling off the solvent; a method comprising extruding a polymerization reaction mixture using an extruder having a vent, while distilling off a solvent through the vent, thereby

obtaining a pelletized polymer; and a method comprising placing a polymerization reaction mixture into hot water and, then, extruding the resultant mixture using an extruder having a vent, while distilling off a solvent and water through the vent, thereby obtaining a pelletized polymer. A most appropriate method can be selected depending on the properties of the cyclic conjugated diene polymer and the solvent used.

Further, examples of ring-opening reactions in the present invention include an ozone oxidation reaction and a nitric acid oxidation reaction.

If desired, depending on the intended use of the final polymer, additives, reinforcing agents and the like, which are used in conventional polymer materials, may be incorporated into the cyclic conjugated diene polymer of the present invention. Examples of such additives and reinforcing agents include stabilizers such as a thermal stabilizer, an antioxidant, and an ultraviolet absorbing agent, a lubricant, a nucleator, a plasticizer, a coloring agent, a pigment, a cross-linking agent, a foaming agent, an antistatic agent, an anti-slip agent, an antiblocking agent, a mold-release agent, another polymer material, and an inorganic reinforcing material (e.g., a glass filler, mineral fiber, and an inorganic filler).

With respect to the stabilizers, such as a thermal stabilizer, an antioxidant, and an ultraviolet absorbing agent, conventional stabilizers may be employed as they are.

5        Examples of thermal stabilizers, antioxidants and ultraviolet absorbing agents include phenol type, organic phosphate type, organic phosphite type, organic amine type and organosulfur type stabilizers.

10       The amount of each of the stabilizers, such as a thermal stabilizer, an antioxidant and an ultraviolet absorbing agent, is generally from 0.001 to 10 wt%, based on the weight of the cyclic conjugated diene polymer.

15       The cyclic conjugated diene polymer of the present invention may be in a single form, or in a composite form with another polymer material (for example, a conventional cyclic conjugated diene polymer), an inorganic reinforcing material or an organic reinforcing material, depending on the intended use of the  
20       polymer.

      When the cyclic conjugated diene polymer of the present invention is intended to be used in a composite form (a resin composition) with another polymer material, such another polymer material may be appropriately  
25       selected from conventional organic polymers. There is

no particular limitation with respect to the type and amount of the organic polymer.

The cyclic conjugated diene polymer of the present invention can be used as an excellent industrial material (e.g., a structural material or a functional material). Specifically, the cyclic conjugated diene polymer of the present invention is useful as a high-performance plastic, a plastic having a wide variety of uses, a special elastomer, a thermoplastic elastomer, an elastic fiber, a sheet, a film, a tube, a hose, an optical material, a coating agent, an insulating agent, a lubricant, a plasticizing agent, a separation membrane, a selective-permeation membrane, a porous membrane, a functional membrane, a vibration-proof material, a noise-proof material, a damping material, a noise insulation material, a functional film (e.g., an electrically conductive film, a photosensitive film), functional beads (e.g., a molecular sieve, a polymer catalyst, a substrate for supporting a polymer catalyst), automobile parts, electric parts, aerospace parts, railroad parts, marine parts, electronic parts, battery parts, parts associated with electronics, parts associated with multi-media devices, a plastic material for batteries, solar battery parts, a functional fiber, a functional sheet, machine parts, a construction



material, a civil engineering material, medical equipment parts, a packaging material for drugs, an encapsulating material for sustained release, a substrate material for a pharmacological substance, a substrate material for a printed circuit, a container for food, a general packaging material, clothes, a material for sports and leisure equipment, a material for general sundries, a material for a tire, a material for a belt, a modifier for other resins, and the like. If desired, a crosslinking agent may be added to the cyclic conjugated diene polymer of the present invention to provide a hardening resin, such as a thermohardening resin, an ultraviolet-hardening resin, an electron radiation-hardening resin, a wet hardening resin, or the like.

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BEST MODE FOR CARRYING OUT THE INVENTION

Hereinbelow, the present invention will be described in more detail with reference to the following Examples and Comparative Examples, but they should not be construed as limiting the scope of the present invention.

In the Examples and Comparative Examples, with respect to chemicals, those which have the highest purity among the commercially available ones were used. With respect to solvents, commercially available solvents were treated by a conventional method before use. That is, the solvents were degassed, dehydrated under reflux over an activated metal in an atmosphere of an inert gas, and purified by distillation.

With respect to measurement of the number average molecular weight ( $\overline{M}_n$ ) and molecular weight distribution ( $\overline{M}_w/\overline{M}_n$  ratio) of a polymer, the measurement was conducted by gel permeation chromatography (GPC), using a liquid chromatograph (HLC-8080) manufactured and sold by Tosoh Corp. Japan, and a column (Showdex : K805+K804+K802) manufactured and sold by Showa Denko K.K., Japan. The number average molecular weight and  $\overline{M}_w/\overline{M}_n$  ratio were obtained, using a calibration curve obtained with respect to a standard polystyrene.

The polymer chain structure of a polymer was

analyzed using an NMR measuring device (JEOL  $\alpha$ -400) manufactured and sold by JEOL LTD, Japan. The measurement frequencies were 400 MHz ( $^1\text{H}$ ) and 100 MHz ( $^{13}\text{C}$ ).

5 For conducting the above NMR measurement, a polymer was dissolved in o-dichlorobenzene- $\text{d}_4$ , to thereby obtain a 10 wt% polymer solution. The measurement temperature was 135 °C. The peak at 1.4 ppm ascribed to cyclohexane was used as a reference peak.

10 The 1,2-bond/1,4-bond molar ratio (the molar ratio of monomer units having a 1,2-bond to monomer units having a 1,4-bond) of a polycyclohexadiene was determined by the method described below.

15 With respect to cyclohexadiene (CHD) monomer units having a 1,2-bond (1,2-CHD monomer units) and CHD monomer units having a 1,4-bond (1,4-CHD monomer units), 1,2-CHD monomer units and 1,4-CHD monomer units are different in the number of protons ( $\text{H}_a$ ) bonded to carbon atoms which neighbor carbon atoms bonded to each other by a double bond (see Fig. 1).

20 1,2-CHD monomer units satisfy the formula  $\text{H}_a/(\text{H}_a+\text{H}_b) = 1/2$ .

1,4-CHD monomer units satisfy the formula  $\text{H}_a/(\text{H}_a+\text{H}_b) = 1/3$ .

25 Therefore, a 1,2-bond/1,4-bond molar ratio with respect to a polymer can be determined by calculating

the proportion of protons which are correlated to carbon atoms which are bonded to each other by a double bond.

5 The 2-D NMR spectrum of a polymer was measured by the H-H COSY method. Cross peaks were observed at from 5.5 ppm to 5.8 ppm which are ascribed to hydrogen atoms bonded to carbon atoms which are bonded to each other by a double bond, and peaks were also observed at from 1.85 ppm to 2.35 ppm which are ascribed to hydrogen  
10 atoms (see Figs. 2 and 3). With respect to the H-H COSY method, reference can be made to, for example, "Kobunshi . Seitaiibunshi no NMR (NMR for polymers and biomolecules)", supervised by Riichiro Chujo, edited by Isao Ando and Yoshio Inoue and published by Tokyo  
15 Kagaku Dozin Co., Ltd., Japan, pp. 31-41 (1992).

Accordingly, it was confirmed that in a molecular chain of the polymer, hydrogen atoms having peaks at 1.85 ppm to 2.35 ppm were those bonded to carbon atoms neighboring carbon atoms which are bonded to each other  
20 by a double bond.

When the molar ratio of 1,2-CHD monomer units to all CHD monomer units is represented by  $\alpha$ , and the ratio ( $H_a/H_a+H_b$ ) of the area of peaks at from 1.85 to 2.35 ppm (ascribed to protons bonded to carbon atoms  
25 neighboring carbon atoms which are bonded to each other

by a double bond) to the area of peaks ascribed to all protons, exclusive of protons bonded to carbon atoms bonded to each other by a double bond, is represented by  $\beta$ ,  $\alpha$  and  $\beta$  satisfy the following formula:

5 
$$1/2 \times \alpha + 1/3(1-\alpha) = \beta.$$

The molar ratio of 1,2-CHD to 1,4-CHD was determined by calculating  $\alpha$  in accordance with the above formula.

The chemical shift of a polymerization catalyst (a complex) was measured using an NMR measuring device (JEOL  $\alpha$ -400) manufactured and sold by JEOL LTD, Japan. The frequencies for measurement were 400 MHz ( $^1\text{H}$ ), 100 MHz ( $^{13}\text{C}$ ), 155 MHz ( $^7\text{Li}$ ) and 58.7 MHz ( $^6\text{Li}$ ).

The chemical shifts of  $^7\text{Li}$  and  $^6\text{Li}$  were measured on the assumption that the peak ascribed to a 1M solution of LiCl in  $\text{D}_2\text{O}$  corresponds to 0 ppm.

The glass transition temperature ( $T_g$ ) of a polymer was measured by the DSC (differential scanning calorimeter) method, using DSC200 manufactured and sold by Seiko Instruments Inc., Japan.

The conversion (mol%) of monomers in a polymerization reaction was calculated by the internal standard method from an absolute amount of monomers remaining in the polymerization reaction mixture, using a gas chromatograph (GC14A) manufactured and sold by Shimadzu Corporation, Japan. Ethylbenzene was used as an inter-

nal standard substance.

Mechanical properties and thermal properties of a polymer were measured in accordance with the following methods.

5           (1) Tensile test (1/8 inch):

The tensile strength (TS) and tensile elongation (TE) of a 1/8-inch thick specimen of a polymer were measured in accordance with ASTM D638.

10           (2) Flexural test (1/8 inch):

The flexural strength (FS) and flexural modulus (FM) of a 1/8-inch thick specimen of a polymer were measured in accordance with ASTM D790.

(3) Izod impact test:

15           The Izod impact strength of a polymer was measured in accordance with ASTM D256 (at room temperature).

(4) Heat distortion temperature (HDT : °C):

20           The heat distortion temperature of a polymer was measured under a load of 1.82 MPa (high load) and under a load of 0.46 MPa (low load) in accordance with ASTM D648.

In the above measurements, the following is to be noted.

1 MPa = 10.20 kg·f/cm<sup>2</sup>; and

1 J/m = 0.102 kg·cm/cm).

25           In the following Examples and Comparative Exam-

ples, for example, a polycyclohexadiene-polyisoprene diblock copolymer is shown simply as a "CHD-*Ip* diblock copolymer". Other block copolymers are also likewise shown.

5     Example 1

(Synthesis of a complex of a Group 1A metal-containing organometallic compound with a first complexing agent)

10     In an atmosphere of dried argon gas, a predetermined amount of N,N,N',N'-tetramethylethylenediamine (TMEDA) to be used as a first complexing agent was dissolved in cyclohexane, to thereby obtain a 1.0 M solution of TMEDA in cyclohexane.

15     Subsequently, the obtained cyclohexane solution of TMEDA was cooled to and maintained at -10 °C. Then, in the atmosphere of dried argon gas, an n-hexane solution of n-butyllithium (n-BuLi) was gradually added to the cyclohexane solution of TMEDA (as the first complexing agent) in an amount such as would provide a Li (in n-  
20     BuLi)/TMEDA molar ratio of 4/2.

It was observed that, upon addition of the n-hexane solution of n-BuLi to the cyclohexane solution of TMEDA, a complex of n-BuLi with TMEDA was quickly formed in the form of white crystals.

25     The resultant mixture containing the complex of

n-BuLi with TMEDA was heated to 70 °C, thereby dissolving the complex in the cyclohexane, and then gradually cooled to -78 °C. As a result, the complex in the form of white (platy) crystals was precipitated.

5           Subsequently, in an atmosphere of dried argon gas, the precipitated complex was separated by filtration. The separated complex was washed with cyclohexane several times, thereby obtaining a final purified complex in the form of white (platy) crystals.

10           The molar ratio of Li (in n-BuLi)/TMEDA in the complex was 4/2 as measured by  $^1\text{H}$ -NMR.

(Polymerization reaction)

15           A well dried 100 ml Schlenk tube was purged with dried argon gas by a conventional method. 27.0 g of cyclohexane was charged in the Schlenk tube. While maintaining the temperature of the cyclohexane at room temperature, the above-obtained complex having a Li (in n-BuLi)/TMEDA molar ratio of 4/2 was added to and dissolved in the cyclohexane in an amount of 0.3 mmol  
20           in terms of the amount of lithium atom, to thereby obtain a complex solution. The complex solution was heated to and maintained at 70 °C.

25           To the above-obtained complex solution was added a 1.0 M solution of TMEDA (as a second complexing agent) in cyclohexane in an amount such that 0.225 mmol of



TMEDA (as the second complexing agent) was added to the complex solution, to thereby obtain a cyclohexane solution of a complex-TMEDA mixture having a Li/TMEDA molar ratio of 4/5.

5           In an atmosphere of dried argon gas, 3.0 g of 1,3-cyclohexadiene (1,3-CHD) was added to the obtained complex-TMEDA mixture solution, and a polymerization reaction was conducted at 70 °C for 1 hour.

10           To the resultant polymerization reaction mixture was added a 10 wt% solution of BHT [2,6-bis(tert-butyl)-4-methylphenol] in methanol, to thereby terminate the polymerization reaction. Then, a large amount of a mixed solvent of methanol and hydrochloric acid was added to the polymerization reaction mixture containing a desired polymer, thereby separating the desired polymer. The separated polymer was washed with methanol and then, dried at 80 °C in vacuo, thereby obtaining a white mass of the polymer in a yield of 100 wt%.

20           The obtained cyclohexadiene (CHD) homopolymer had a number average molecular weight as high as 9,700 and an  $\overline{M}_w/\overline{M}_n$  ratio (criterion for molecular weight distribution) of 1.28.

25           With respect to the obtained polymer, the 1,2-bond/1,4-bond molar ratio (i.e., the molar ratio of

cyclic conjugated diene monomer units having a 1,2-bond to cyclic conjugated diene monomer units having a 1,4-bond) was 61/39. The glass transition temperature ( $T_g$ ) of the obtained polymer was 158 °C as measured in accordance with the DSC method.

#### Example 2

A well dried 100 ml Schlenk tube was purged with dried argon gas by a conventional method. 27.0 g of cyclohexane was charged in the Schlenk tube. While maintaining the temperature of the cyclohexane at 40 °C, a 1.6 M solution of n-BuLi in n-hexane was added to and dissolved in the cyclohexane in an amount of 0.3 mmol in terms of the amount of lithium atom, to thereby obtain a solution. The obtained solution was agitated for 10 minutes.

To the above-obtained solution was added a 1.0 M solution of TMEDA (as a first complexing agent) in cyclohexane in an amount such as would provide a Li (in n-BuLi)/TMEDA molar ratio of 4/2, and a reaction was conducted at 40 °C for 10 minutes, to thereby obtain a complex solution. The obtained complex solution was heated to and maintained at 70 °C.

To the above-obtained complex solution was added a 1.0 M solution of TMEDA (as a second complexing agent) in cyclohexane in an amount such that 0.225 mmol of

TMEDA (as the second complexing agent) was added to the complex solution, to thereby obtain a cyclohexane solution of a complex-TMEDA mixture having a Li/TMEDA molar ratio of 4/5.

5           To the obtained complex-TMEDA mixture solution was added 3.0 g of 1,3-cyclohexadiene (1,3-CHD) in an atmosphere of dried argon gas, and a polymerization reaction was conducted at 70 °C for 1 hour.

10           To the resultant polymerization reaction mixture was added a 10 wt% solution of BHT [2,6-bis(tert-butyl)-4-methylphenol] in methanol, to thereby terminate the polymerization reaction. Then, a large amount of a mixed solvent of methanol and hydrochloric acid was added to the polymerization reaction mixture containing a desired polymer, thereby separating the  
15           desired polymer. The separated polymer was washed with methanol and then, dried at 80 °C in vacuo, thereby obtaining a white mass of the polymer in a yield of 100 wt%.

20           The obtained CHD homopolymer had a number average molecular weight as high as 9,300 and an  $\overline{M}_w/\overline{M}_n$  ratio (criterion for molecular weight distribution) of 1.36.

25           With respect to the obtained polymer, the 1,2-bond/1,4-bond molar ratio (i.e., the molar ratio of

cyclic conjugated diene monomer units having a 1,2-bond to cyclic conjugated diene monomer units having a 1,4-bond) was 51/49. The glass transition temperature ( $T_g$ ) of the obtained polymer was 152 °C as measured in accordance with the DSC method.

#### Comparative Example 1

A well dried 100 ml Schlenk tube was purged with dried argon gas by a conventional method. 27.0 g of cyclohexane was charged in the Schlenk tube. While maintaining the temperature of the cyclohexane at room temperature, a 1.6 M solution of n-BuLi in n-hexane was added to the cyclohexane in an amount of 0.30 mmol in terms of the amount of lithium atom to thereby obtain a solution. The obtained solution was agitated for 10 minutes.

To the above-obtained solution was added 3.0 g of 1,3-cyclohexadiene (1,3-CHD) in an atmosphere of dried argon gas, and a polymerization reaction was conducted at room temperature for 6 hours. After the addition of 1,3-CHD, the color, which is characteristic of the anion, quickly disappeared from the mixture.

To the resultant polymerization reaction mixture was added a 10 wt% solution of BHT [2,6-bis(tert-butyl)-4-methylphenol] in methanol, to thereby terminate the polymerization reaction. Then, a large amount

of a mixed solvent of methanol and hydrochloric acid was added to the polymerization reaction mixture containing a desired polymer, thereby separating the desired polymer. The separated polymer was washed with  
5 methanol and then, dried at 80 °C in vacuo, thereby obtaining a mass of the polymer in a yield as low as 23 wt%.

The obtained cyclohexadiene (CHD) homopolymer had a number average molecular weight of 3,200 and an  
10  $\overline{M}_w/\overline{M}_n$  ratio (criterion for molecular weight distribution) of 2.89. With respect to the obtained polymer, the 1,2-bond/1,4-bond molar ratio (i.e., the molar ratio of cyclic conjugated diene monomer units having a  
1,2-bond to cyclic conjugated diene monomer units  
15 having a 1,4-bond) was 5/95. The glass transition temperature ( $T_g$ ) of the obtained polymer was as low as 88 °C as measured in accordance with the DSC method.

#### Comparative Example 2

A well dried 100 ml Schlenk tube was purged with  
20 dried argon gas by a conventional method. 27.0 g of cyclohexane was charged in the Schlenk tube. While maintaining the temperature of the cyclohexane at 40 °C, a 1.6 M solution of n-BuLi in n-hexane was added to the cyclohexane in an amount of 0.30 mmol in terms  
25 of the amount of lithium atom to thereby obtain a

solution. The obtained solution was agitated for 10 minutes.

To the above-obtained solution was added 3.0 g of 1,3-cyclohexadiene (1,3-CHD) in an atmosphere of dried argon gas, and a polymerization reaction was conducted at 40 °C for 6 hours. After the addition of 1,3-CHD, the color, which is characteristic of the anion, quickly disappeared from the mixture.

To the resultant polymerization reaction mixture was added a 10 wt% solution of BHT [2,6-bis(tert-butyl)-4-methylphenol] in methanol, to thereby terminate the polymerization reaction. Then, a large amount of a mixed solvent of methanol and hydrochloric acid was added to the polymerization reaction mixture containing a desired polymer, thereby separating the desired polymer. The separated polymer was washed with methanol and then, dried at 80 °C in vacuo, thereby obtaining a mass of the polymer in a yield as low as 20 wt%.

The obtained cyclohexadiene (CHD) homopolymer had a number average molecular weight of 2,920 and an  $M_w/M_n$  ratio (criterion for molecular weight distribution) of 2.92. With respect to the obtained polymer, the 1,2-bond/1,4-bond molar ratio (i.e., the molar ratio of cyclic conjugated diene monomer units having a

1,2-bond to cyclic conjugated diene monomer units having a 1,4-bond) was 2/98. The glass transition temperature ( $T_g$ ) of the obtained polymer was as low as 87 °C as measured in accordance with the DSC method.

5     Examples 3 to 6

          A well dried 100 ml Schlenk tube was purged with dried argon gas by a conventional method. 27.0 g of cyclohexane was charged in the Schlenk tube. While maintaining the temperature of the cyclohexane at room  
10     temperature, a complex having a Li (in n-BuLi)/TMEDA molar ratio of 4/2 which was obtained in substantially the same manner as in Example 1 was added to and dissolved in the cyclohexane in an amount of 0.15 mmol in terms of the amount of lithium atom, to thereby obtain  
15     a complex solution. The complex solution was heated to and maintained at 40 °C.

          In Examples 3 to 6, 1.0 M solutions of TMEDA in cyclohexane were individually added to the above-obtained complex solution in respective amounts such that  
20     0.0375 mmol, 0.0750 mmol, 0.1125 mmol and 0.150 mmol of TMEDA (as a second complexing agent) were individually added to the complex solution, to thereby obtain cyclohexane solutions of complex-TMEDA mixtures having  
       respective Li/TMEDA molar ratios of 4/3, 4/4, 4/5 and  
25     4/6.

In an atmosphere of dried argon gas, 3.0 g of 1,3-cyclohexadiene (1,3-CHD) was added to the individual complex-TMEDA mixture solutions obtained above, and polymerization reactions were conducted at 40 °C for 4 hours. After that period of time, a 10 wt% solution of BHT [2,6-bis(tert-butyl)-4-methylphenol] in methanol was added to the individual resultant polymerization reaction mixtures, to thereby terminate the polymerization reactions. Then, a large amount of a mixed solvent of methanol and hydrochloric acid was added to the individual polymerization reaction mixtures containing desired polymers, thereby separating the desired polymers. The separated polymers were individually washed with methanol and then, dried at 80 °C in vacuo, thereby obtaining masses of the polymers, each in a yield of 100 wt%.

With respect to the obtained polymers, respective 1,2-bond/1,4-bond molar ratios (i.e., molar ratios of cyclic conjugated diene monomer units having a 1,2-bond to cyclic conjugated diene monomer units having a 1,4-bond) were 48/52, 51/49, 52/48 and 54/46.

#### Comparative Examples 3 to 6

A well dried 100 ml Schlenk tube was purged with dried argon gas by a conventional method. 27.0 g of cyclohexane was charged in the Schlenk tube. While



maintaining the temperature of the cyclohexane at room temperature, a 1.6 M solution of n-BuLi in n-hexane was added to the cyclohexane in an amount of 0.15 mmol in terms of the amount of lithium atom, to thereby obtain  
5 a solution. The obtained solution was heated to and maintained at 40 °C.

In Comparative Examples 3 to 6, 1.0 M solutions of TMEDA in cyclohexane were individually added to the above-obtained solution in respective amounts such that  
10 0.0047 mmol, 0.0094 mmol and, 0.0188 mmol and 0.0375 mmol of TMEDA were individually added to the solution and agitated for 10 minutes, to thereby obtain mixtures containing complexes of n-BuLi with TMEDA having respective Li/TMEDA molar ratios of  
15 4/0.125, 4/0.25, 4/0.5 and 4/1, respectively.

In an atmosphere of dried argon gas, 3.0 g of 1,3-cyclohexadiene (1,3-CHD) was added to the individual mixtures obtained above, and polymerization reactions were conducted at 40 °C for 4 hours. After that  
20 period of time, a 10 wt% solution of BHT [2,6-bis(tert-butyl)-4-methylphenol] in methanol was added to the individual resultant polymerization reaction mixtures, to thereby terminate the polymerization reactions. Then, a large amount of a mixed solvent of  
25 methanol and hydrochloric acid was added to the indi-

vidual polymerization reaction mixtures containing desired polymers, thereby separating the desired polymers. The separated polymers were washed with methanol and then, dried at 80 °C in vacuo, thereby obtaining masses of the polymers.

With respect to the obtained polymers, respective 1,2-bond/1,4-bond molar ratios (i.e., molar ratios of cyclic conjugated diene monomer units having a 1,2-bond to cyclic conjugated diene monomer units having a 1,4-bond) were 6/94, 9/91, 21/79 and 29/71.

#### Example 7

A well dried 100 ml Schlenk tube was purged with dried argon gas by a conventional method. 27.0 g of cyclohexane was charged in the Schlenk tube. While maintaining the temperature of the cyclohexane at room temperature, a 1.6 M solution of n-BuLi in n-hexane was added to and dissolved in the cyclohexane in an amount of 0.30 mmol in terms of the amount of lithium atom to thereby obtain a solution. The obtained solution was agitated for 10 minutes.

To the above-obtained solution was added a 1.0 M solution of N,N,N',N'-tetramethylpropylenediamine (TMPDA) (as a first complexing agent) in cyclohexane in an amount such as would provide a Li (in n-BuLi)/TMPDA molar ratio of 4/2, and a reaction was conducted at

room temperature for 10 minutes, to thereby obtain a complex solution. The complex solution was heated to and maintained at 40 °C.

To the above-obtained complex solution was added a  
5 1.0 M solution of TMPDA (as a second complexing agent) in cyclohexane in an amount such that 0.225 mmol of TMPDA (as the second complexing agent) was added to the complex solution, to thereby obtain a cyclohexane solution of a complex-TMPDA mixture having a Li/TMPDA  
10 molar ratio of 4/5.

To the obtained complex-TMPDA mixture solution was added 3.0 g of 1,3-cyclohexadiene (1,3-CHD) in an atmosphere of dried argon gas, and a polymerization reaction was conducted at 40 °C for 4 hours. To the  
15 resultant polymerization reaction mixture was added a 10 wt% solution of BHT [2,6-bis(tert-butyl)-4-methylphenol] in methanol, to thereby terminate the polymerization reaction. Then, a large amount of a mixed solvent of methanol and hydrochloric acid was added to  
20 the polymerization reaction mixture containing a desired polymer, thereby separating the desired polymer. The separated polymer was washed with methanol and then, dried at 80 °C in vacuo, thereby obtaining a mass of the polymer in a yield of 100 wt%.

25 With respect to the obtained polymer, the 1,2-

bond/1,4-bond molar ratio (i.e., the molar ratio of cyclic conjugated diene monomer units having a 1,2-bond to cyclic conjugated diene monomer units having a 1,4-bond) was 47/53.

5     Examples 8 to 12

10     A well dried 100 ml Schlenk tube was purged with dried argon gas by a conventional method. 20.0 g of cyclohexane was charged in the Schlenk tube. While maintaining the temperature of the cyclohexane at room temperature, a complex having a Li (in n-BuLi)/TMEDA molar ratio of 4/2 which was obtained in substantially the same manner as in Example 1 was added to and dissolved in the cyclohexane in an amount of 0.07 mmol in terms of the amount of lithium atom, to thereby obtain  
15     a complex solution. The complex solution was heated to and maintained at 60 °C.

20     To the above-obtained complex solution were individually added 1.0 M solutions of TMEDA in cyclohexane in respective amounts such that TMEDA (as a second complexing agent) was added to the complex solution in the respective amounts shown in Table 1, to thereby obtain cyclohexane solutions of complex-TMEDA mixtures having various Li/TMEDA molar ratios.

25     In an atmosphere of dried argon gas, 3.0 g of 1,3-cyclohexadiene (1,3-CHD) was added to the obtained

individual complex-TMEDA mixture solutions, and polymerization reactions were conducted at 60 °C for 4 hours.

5 After that period of time, a 10 wt% solution of BHT [2,6-bis(tert-butyl)-4-methylphenol] in methanol was added to the resultant polymerization reaction mixtures, to thereby terminate the polymerization reactions. Then, a large amount of a mixed solvent of methanol and hydrochloric acid was added to the indi-  
10 vidual polymerization reaction mixtures containing desired polymers, thereby separating the desired polymers. The separated polymers were individually washed with methanol and then, dried at 80 °C in vacuo, thereby obtaining white masses of the polymers, each in a  
15 yield of 100 wt%.

With respect to the obtained polymers, respective 1,2-bond/1,4-bond molar ratios (i.e., molar ratios of cyclic conjugated diene monomer units having a 1,2-bond to cyclic conjugated diene monomer units having a 1,4-  
20 bond) were 44/56, 52/48, 54/46, 56/44 and 60/40.

Results are shown in Table 1.

Table 1

	Second complexing agent		Yield (wt%)
	Type	Amount (mmol)	
Example 8	TMEDA	0.007	100
Example 9	TMEDA	0.035	100
Example 10	TMEDA	0.070	100
Example 11	TMEDA	0.140	100
Example 12	TMEDA	0.210	100

Comparative Example 7

A well dried 100 ml Schlenk tube was purged with dried argon gas by a conventional method. 27.0 g of cyclohexane was charged in the Schlenk tube. While maintaining the temperature of the cyclohexane at room temperature, a 1.6 M solution of n-BuLi in n-hexane was added to the cyclohexane in an amount of 0.15 mmol in terms of the amount of lithium atom to thereby obtain a solution. The obtained solution was heated to and maintained at 60 °C, and was agitated for 10 minutes.

To the resultant solution was added 3.0 g of 1,3-cyclohexadiene (1,3-CHD) in an atmosphere of dried argon gas, and a polymerization reaction was conducted at 60 °C for 4 hours. After the addition of 1,3-CHD monomers, the color, which is characteristic of the

cyclohexadienyl anion, quickly disappeared from the mixture. In the reaction, a desired polymer was not obtained.

Example 13

5           A well dried 100 ml Schlenk tube was purged with dried argon gas by a conventional method. 27.0 g of cyclohexane was charged in the Schlenk tube. While maintaining the temperature of the cyclohexane at room temperature, a 1.6 M solution of n-BuLi in n-hexane was  
10           added to and dissolved in the cyclohexane in an amount of 0.15 mmol in terms of the amount of lithium atom to thereby obtain a solution. The obtained solution was agitated for 10 minutes.

          To the resultant solution was added a 1.0 M solution of TMEDA (as a first complexing agent) in cyclohexane in an amount such as would provide a Li (in n-BuLi)/TMEDA molar ratio of 4/2, and a reaction was  
15           conducted at room temperature for 10 minutes, to thereby obtain a complex solution. The complex solution was heated to and maintained at 40 °C.  
20

          To the above-obtained complex solution was added a 1.0 M solution of TMEDA (as a second complexing agent) in cyclohexane in an amount such that 0.1125 mmol of TMEDA (as the second complexing agent) was added to the  
25           complex solution, to thereby obtain a cyclohexane

solution of a complex-TMEDA mixture having a Li/TMEDA molar ratio of 4/5.

To the obtained complex-TMEDA mixture solution was added 3.0 g of 1,3-cyclohexadiene (1,3-CHD) in an atmosphere of dried argon gas, and a polymerization reaction was conducted at 40 °C for 4 hours.

To the resultant polymerization reaction mixture was added a 10 wt% solution of BHT [2,6-bis(tert-butyl)-4-methylphenol] in methanol, to thereby terminate the polymerization reaction. Then, a large amount of a mixed solvent of methanol and hydrochloric acid was added to the polymerization reaction mixture containing a desired polymer, thereby separating the desired polymer. The separated polymer was washed with methanol and then, dried at 80 °C in vacuo, thereby obtaining a white mass of the polymer in a yield of 100 wt%.

The obtained CHD homopolymer had a number average molecular weight as high as 19,750 and an  $\overline{M}_w/\overline{M}_n$  ratio (criterion for molecular weight distribution) of 1.09.

With respect to the obtained polymer, the 1,2-bond/1,4-bond molar ratio (i.e., the molar ratio of cyclic conjugated diene monomer units having a 1,2-bond to cyclic conjugated diene monomer units having a 1,4-



bond) was 50/50. The glass transition temperature ( $T_g$ ) of the obtained polymer was 156 °C as measured in accordance with the DSC method.

#### Example 14

5           A polymerization reaction was conducted in substantially the same manner as in Example 13, except that the reaction temperature of the reaction of n-BuLi with TMEDA was 60 °C.

10           The obtained cyclohexadiene (CHD) homopolymer had a number average molecular weight as high as 20,800 and an  $\overline{M}_w/\overline{M}_n$  ratio (criterion for molecular weight distribution) of 1.26.

15           With respect to the obtained polymer, the 1,2-bond/1,4-bond molar ratio (i.e., the molar ratio of cyclic conjugated diene monomer units having a 1,2-bond to cyclic conjugated diene monomer units having a 1,4-bond) was 52/48. The glass transition temperature ( $T_g$ ) of the obtained polymer was 155 °C as measured in accordance with the DSC method.

#### 20           Example 15

          A polymerization reaction was conducted in substantially the same manner as in Example 13, except that the reaction temperature of the reaction of n-BuLi with TMEDA was 40 °C.

25           The obtained cyclohexadiene (CHD) homopolymer had

a number average molecular weight as high as 20,060 and an  $\overline{M}_w/\overline{M}_n$  ratio (criterion for molecular weight distribution) of 1.14.

5 With respect to the obtained polymer, the 1,2-bond/1,4-bond molar ratio (i.e., the molar ratio of cyclic conjugated diene monomer units having a 1,2-bond to cyclic conjugated diene monomer units having a 1,4-bond) was 54/46. The glass transition temperature ( $T_g$ ) of the obtained polymer was 159 °C as measured in  
10 accordance with the DSC method.

Comparative Example 8

A well dried 100 ml Schlenk tube was purged with dried argon gas by a conventional method. 27.0 g of cyclohexane was charged in the Schlenk tube. While  
15 maintaining the temperature of the cyclohexane at room temperature, a 1.6 M solution of n-BuLi in n-hexane was added to the cyclohexane in an amount of 0.15 mmol in terms of the amount of lithium atom to thereby obtain a solution. The obtained solution was agitated for 10  
20 minutes.

To the obtained solution was added 3.0 g of 1,3-cyclohexadiene (1,3-CHD) in an atmosphere of dried argon gas, and a polymerization reaction was conducted at room temperature for 6 hours. After the addition of  
25 1,3-CHD, the color, which is characteristic of the

anion, quickly disappeared from the mixture.

To the resultant polymerization reaction mixture was added a 10 wt% solution of BHT [2,6-bis(tert-butyl)-4-methylphenol] in methanol, to thereby terminate the polymerization reaction. Then, a large amount of a mixed solvent of methanol and hydrochloric acid was added to the polymerization reaction mixture containing a desired polymer, thereby separating the desired polymer. The separated polymer was washed with methanol and then, dried at 80 °C in vacuo, thereby obtaining a mass of the polymer in a yield as low as 18 wt%.

The obtained cyclohexadiene (CHD) homopolymer had a number average molecular weight as low as 2,750 and an  $\overline{M}_w/\overline{M}_n$  ratio (criterion for molecular weight distribution) of 3.19.

With respect to the obtained polymer, the 1,2-bond/1,4-bond molar ratio (i.e., the molar ratio of cyclic conjugated diene monomer units having a 1,2-bond to cyclic conjugated diene monomer units having a 1,4-bond) was 2/98. The glass transition temperature ( $T_g$ ) of the obtained polymer was as low as 87 °C as measured in accordance with the DSC method.

#### Example 16

A well dried 300 ml pressure-resistant glass

bottle was purged with dried argon gas by a conventional method. 120.0 g of cyclohexane was charged in the glass bottle. While maintaining the temperature of the cyclohexane at room temperature, a 1.6 M solution of n-BuLi in n-hexane was added to the cyclohexane in an amount of 3.0 mmol in terms of the amount of lithium atom. The resultant mixture was agitated for 10 minutes.

Subsequently, a 1.0 M solution of TMEDA (as a first complexing agent) in cyclohexane was added to the above mixture so as to provide a Li (in n-BuLi)/TMEDA molar ratio of 4/2, and a reaction was conducted at room temperature for 10 minutes to thereby form a complex of n-BuLi with TMEDA. The resultant mixture containing the complex of n-BuLi with TMEDA was heated to and maintained at 40 °C, to thereby obtain a complex solution.

To the above-obtained complex solution was added a 1.0 M solution of TMEDA (as a second complexing agent) in cyclohexane in an amount such that 2.25 mmol of TMEDA (as the second complexing agent) was added to the complex solution, to thereby obtain a cyclohexane solution of a complex-TMEDA mixture having a Li/TMEDA molar ratio of 4/5.

In an atmosphere of dried argon gas, 4.5 g of

1,3-CHD was added to the obtained complex-TMEDA mixture solution, and a polymerization reaction was conducted at 40 °C for 1 hour.

5 To the resultant polymerization reaction mixture was added 21.0 g of isoprene (Ip) in an atmosphere of dried argon gas, and a polymerization reaction was further conducted at 40 °C for 1 hour to thereby form a CHD-*Ip* diblock copolymer.

10 To the resultant polymerization reaction mixture containing the CHD-*Ip* diblock copolymer was added 4.5 g of 1,3-CHD in an atmosphere of dried argon gas, and a polymerization reaction was further conducted at 40 °C for 2 hours to thereby form a CHD-*Ip*-CHD triblock copolymer.

15 To the resultant polymerization reaction mixture was added a 10 wt% solution of BHT [2,6-bis(tert-butyl)-4-methylphenol] in methanol, to thereby terminate the polymerization reaction. Then, a large amount of a mixed solvent of methanol and hydrochloric acid  
20 was added to the polymerization reaction mixture containing the CHD-*Ip*-CHD triblock copolymer to thereby separate the triblock copolymer. The separated triblock copolymer was washed with methanol and then, dried at 60 °C in vacuo to thereby obtain a viscous  
25 form of the CHD-*Ip*-CHD triblock copolymer in a yield of

100 wt%.

The obtained CHD-*Ip*-CHD triblock copolymer had a number average molecular weight as high as 9,890 and an  $\overline{M}_w/\overline{M}_n$  ratio of 1.04.

5        The polymer chain structure of the copolymer was determined by  $^1\text{H-NMR}$ . It was confirmed that the polymer chain of the copolymer had substantially the same ratio of cyclic conjugated diene monomer units as the ratio of cyclic conjugated diene monomers charged in  
10       the glass bottle.

With respect to the obtained copolymer, the 1,2-bond/1,4-bond molar ratio was 43/57.

Example 17

15       A well dried 300 ml pressure-resistant glass bottle was purged with dried argon gas by a conventional method. 120.0 g of cyclohexane was charged in the glass bottle. While maintaining the temperature of the cyclohexane at room temperature, a 1.1 M solution of *s*-BuLi in *n*-hexane was added to the cyclohexane in an  
20       amount of 3.0 mmol in terms of the amount of lithium atom. The resultant mixture was agitated for 10 minutes.

Subsequently, a 1.0 M solution of TMEDA (as a first complexing agent) in cyclohexane was added to the  
25       above mixture so as to provide a Li (in *s*-BuLi)/TMEDA

molar ratio of 4/2, and a reaction was conducted at room temperature for 10 minutes to thereby form a complex of s-BuLi with TMEDA. The resultant mixture containing the complex of s-BuLi with TMEDA was heated to and maintained at 40 °C, to thereby obtain a complex solution.

To the above-obtained complex solution, which had a blue color, was added a 1.0 M solution of TMEDA (as a second complexing agent) in cyclohexane in an amount such that 2.25 mmol of TMEDA (as the second complexing agent) was added to the complex solution, to thereby obtain a cyclohexane solution of a complex-TMEDA mixture having a Li/TMEDA molar ratio of 4/5.

To the obtained complex-TMEDA mixture solution, which had a blue color, was added 1.5 mmol of m-diisopropenylbenzene (m-DIPB) to thereby obtain a mixture. After the blue color of the mixture, which indicates the presence of radicals, changed to orange, which indicates the absence of radicals, 21.0 g of isoprene (Ip) was added to the above mixture, and a polymerization reaction was conducted at 40 °C for 1 hour to thereby form an Ip-containing copolymer.

To the resultant polymerization reaction mixture containing the Ip-containing copolymer was added 9.0 g of 1,3-CHD in an atmosphere of dried argon gas, and a

polymerization reaction was further conducted at 40 °C for 2 hours to thereby form a CHD-Ip-CHD triblock copolymer.

5 To the resultant polymerization reaction mixture was added a 10 wt% solution of BHT [2,6-bis(tert-butyl)-4-methylphenol] in methanol, to thereby terminate the polymerization reaction. Then, a large amount of a mixed solvent of methanol and hydrochloric acid was added to the polymerization reaction mixture containing the CHD-Ip-CHD triblock copolymer, thereby separating the triblock copolymer. The separated triblock copolymer was washed with methanol and then, dried at 60 °C in vacuo, thereby obtaining an elastic form of the CHD-Ip-CHD triblock copolymer in a yield of 100 wt%.  
10  
15

The obtained CHD-Ip-CHD triblock copolymer had a number average molecular weight as high as 19,890 and an  $\overline{M}_w/\overline{M}_n$  ratio of 1.34.

20 The polymer chain structure of the triblock copolymer was determined by  $^1\text{H-NMR}$ . It was confirmed that the polymer chain of the triblock copolymer had substantially the same ratio of cyclic conjugated diene monomer units as the ratio of cyclic conjugated diene monomers charged in the glass bottle.

25 With respect to the obtained triblock copolymer,



the 1,2-bond/1,4-bond molar ratio was 46/54.

Example 18

5 A well dried 100 ml Schlenk tube was purged with  
dried argon gas by a conventional method. 27.0 g of  
cyclohexane was charged in the Schlenk tube. While  
maintaining the temperature of the cyclohexane at room  
temperature, a 1.6 M solution of n-BuLi in n-hexane was  
added to and dissolved in the cyclohexane in an amount  
of 0.07 mmol in terms of the amount of lithium atom to  
10 thereby obtain a solution. The obtained solution was  
agitated for 10 minutes.

To the resultant solution was added a 1.0 M solu-  
tion of TMEDA (as a first complexing agent) in cyclo-  
hexane in an amount such as would provide a Li (in n-  
15 BuLi)/TMEDA molar ratio of 4/2, and a reaction was  
conducted at room temperature for 10 minutes, to there-  
by obtain a complex solution. The complex solution was  
heated to and maintained at 40 °C.

To the above-obtained complex solution was added a  
20 1.0 M solution of TMEDA (as a second complexing agent)  
in cyclohexane in an amount such that 0.0525 mmol of  
TMEDA (as the second complexing agent) was added to the  
complex solution, to thereby obtain a cyclohexane  
solution of a complex-TMEDA mixture having a Li/TMEDA  
25 molar ratio of 4/5.

To the obtained complex-TMEDA mixture solution was added 3.0 g of 1,3-cyclohexadiene (1,3-CHD) in an atmosphere of dried argon gas, and a polymerization reaction was conducted at 40 °C for 6 hours.

5 To the resultant polymerization reaction mixture was added a 10 wt% solution of BHT [2,6-bis(tert-butyl)-4-methylphenol] in methanol, to thereby terminate the polymerization reaction. Then, a large amount of a mixed solvent of methanol and hydrochloric acid  
10 was added to the polymerization reaction mixture containing a desired polymer, thereby separating the desired polymer. The separated polymer was washed with methanol and then, dried at 80 °C in vacuo, thereby obtaining a white mass of the polymer in a yield of  
15 100 wt%.

The obtained CHD homopolymer had a number average molecular weight as high as 44,800 and an  $M_w/M_n$  ratio (criterion for molecular weight distribution) of 1.21.

20 With respect to the obtained polymer, a 1,2-bond/1,4-bond molar ratio (i.e., a molar ratio of cyclic conjugated diene monomer unit having a 1,2-bond to cyclic conjugated diene monomer unit having a 1,4-bond) was 51/49. The glass transition temperature ( $T_g$ )  
25 of the obtained polymer was 165 °C as measured in

accordance with the DSC method.

The tensile modulus (TM) of the obtained polymer was 4,612 MPa (1 MPa = 10.20 kg·f/cm<sup>2</sup>).

Example 19

5           A well dried 100 ml Schlenk tube was purged with  
dried argon gas by a conventional method. 1 g of the  
polymer obtained in Example 18 and 50 ml of trichloro-  
benzene were charged in the Schlenk tube. In an atmos-  
phere of dried argon gas, the resultant mixture was  
10           heated to 150 °C under agitation, thereby dissolving  
the polymer in the trichlorobenzene.

          To the resultant polymer solution was added tetra-  
chloro-1,4-benzoquinone (p-chloranil) in an amount of 4  
equivalents per equivalent of cyclohexene units in the  
15           polymer. A dehydrogenation reaction was conducted at  
150 °C for 20 hours. After completion of the reaction,  
removal of the solvent was conducted by a conventional  
method, thereby obtaining a light yellow dehydrogenated  
polymer.

20           The UV spectrum of the obtained dehydrogenated  
polymer was measured. It was confirmed that, in the  
dehydrogenated cyclic conjugated diene polymer, 72 % of  
the cyclohexene units in the polymer obtained in Exam-  
ple 18 had been converted to benzene rings.

25           Example 20

A well dried 5-liter high-pressure autoclave having an electromagnetic induction agitator was purged with dried nitrogen gas by a conventional method.

In an atmosphere of dried nitrogen gas, 2,700 g of cyclohexane was charged in the autoclave. The temperature of the cyclohexane was maintained at room temperature.

n-BuLi was added to the autoclave in an amount of 15.0 mmol in terms of the amount of lithium atom. To the resultant cyclohexane solution of n-BuLi was added 7.5 mmol of TMEDA (as a first complexing agent), and the resultant mixture was agitated at room temperature for 10 minutes.

The temperature of the autoclave was elevated to 60 °C, and then, 11.25 mmol of TMEDA (as a second complexing agent) was added to the above-obtained mixture.

300 g of 1,3-CHD was charged in the autoclave, and a polymerization reaction was conducted at 60 °C for 3 hours. After that period of time, the conversion of 1,3-CHD was 99.8 mol% as measured by gas chromatography.

The polymerization reaction mixture was transferred by pressure to another 5-liter high-pressure autoclave having an electromagnetic induction agitator,

which autoclave had been well dried by a conventional method. Dehydrated n-heptanol was added to the polymerization reaction mixture in an equimolar amount to the amount of lithium atoms present in the polymerization reaction mixture, to thereby terminate the polymerization reaction. To the polymerization reaction mixture was added a stabilizing agent [Irganox B215 (0037HX)] manufactured and sold by CIBA GEIGY, Switzerland, and then removal of the solvent was conducted by a conventional method, thereby obtaining a CHD homopolymer.

The number average molecular weight of the obtained polymer was 20,100. The  $\overline{M}_w/\overline{M}_n$  ratio was 1.27.

The 1,2-bond/1,4-bond molar ratio was 48/52. The glass transition temperature ( $T_g$ ) was 151 °C as measured in accordance with the DSC method.

#### Example 21

A well dried 5-liter high-pressure autoclave having an electromagnetic induction agitator was purged with dried nitrogen gas by a conventional method.

In an atmosphere of dried nitrogen gas, 2,700 g of cyclohexane was charged in the autoclave. The temperature of the cyclohexane was maintained at 60 °C.

n-BuLi was added to the autoclave in an amount of 15.0 mmol in terms of the amount of lithium atom. To

the resultant cyclohexane solution of n-BuLi was added 7.5 mmol of TMEDA (as a first complexing agent), and the resultant mixture was agitated at 60 °C for 10 minutes.

5 While maintaining the temperature of the autoclave at 60 °C, 11.25 mmol of TMEDA (as a second complexing agent) was added to the above-obtained mixture.

300 g of 1,3-CHD was charged in the autoclave, and a polymerization reaction was conducted at 60 °C for 3 10 hours. After that period of time, the conversion of 1,3-CHD was 99.2 mol% as measured by gas chromatography.

15 The polymerization reaction mixture was transferred by pressure to another 5-liter high-pressure autoclave having an electromagnetic induction agitator, which autoclave had been well dried by a conventional method. Dehydrated n-heptanol was added to the polymerization reaction mixture in an equimolar amount to the amount of lithium atoms present in the polymeri- 20 zation reaction mixture, to thereby terminate the polymerization reaction. To the polymerization reaction mixture was added a stabilizing agent [Irganox B215 (0037HX)] manufactured and sold by CIBA GEIGY, 25 Switzerland, and then removal of the solvent was conducted by a conventional method, thereby obtaining a

CHD homopolymer.

The number average molecular weight of the obtained polymer was 20,500. The  $\overline{M}_w/\overline{M}_n$  ratio was 1.29.

5 The 1,2-bond/1,4-bond molar ratio was 50/50. The glass transition temperature ( $T_g$ ) was 152 °C as measured in accordance with the DSC method.

Example 22

10 A well dried 5-liter high-pressure autoclave having an electromagnetic induction agitator was purged with dried nitrogen gas by a conventional method.

In an atmosphere of dried nitrogen gas, 2,700 g of cyclohexane was charged in the autoclave. The temperature of the cyclohexane was maintained at room temperature.

15 n-BuLi was added to the autoclave in an amount of 15.0 mmol in terms of the amount of lithium atom. To the resultant cyclohexane solution of n-BuLi was added 7.5 mmol of TMEDA (as a first complexing agent), and the resultant mixture was agitated at room temperature  
20 for 10 minutes.

The temperature of the autoclave was elevated to 40 °C, and then, 11.25 mmol of TMEDA (as a second complexing agent) was added to the above-obtained mixture.

25 300 g of 1,3-CHD was charged in the autoclave, and

a polymerization reaction was conducted at 40 °C for 4 hours. After that period of time, the conversion of 1,3-CHD was 99.6 mol% as measured by gas chromatography.

5 The polymerization reaction mixture was transferred by pressure to another 5-liter high-pressure autoclave having an electromagnetic induction agitator, which autoclave had been well dried by a conventional method. Dehydrated n-heptanol was added to the polymerization reaction mixture in an equimolar amount  
10 relative to the amount of lithium atoms present in the polymerization reaction mixture, to thereby terminate the polymerization reaction. To the polymerization reaction mixture was added a stabilizing agent [Irganox B215 (0037HX)] manufactured and sold by CIBA GEIGY,  
15 Switzerland, and then removal of the solvent was conducted by a conventional method, thereby obtaining a CHD homopolymer.

20 The number average molecular weight of the obtained polymer was 20,200. The  $\overline{M}_w/\overline{M}_n$  ratio was 1.23.

The 1,2-bond/1,4-bond molar ratio was 61/39. The glass transition temperature ( $T_g$ ) was 158 °C as measured in accordance with the DSC method.

#### Example 23

25 A well dried 5-liter high-pressure autoclave



having an electromagnetic induction agitator was purged with dried nitrogen gas by a conventional method.

In an atmosphere of dried nitrogen gas, 1,500 g of cyclohexane was charged in the autoclave. The temperature of the cyclohexane was maintained at 70 °C.

1,500 g of a 10 wt% cyclohexane solution of the polymer obtained in Example 22 was added to the autoclave. To the resultant polymer solution was added a catalyst solution, which was prepared by adding titanocene dichloride (TC) and diisobutyl aluminum hydride (DIBAL-H) to cyclohexane (TC/DIBAL-H molar ratio : 1/6), as a hydrogenation catalyst, in an amount of 290 ppm, in terms of the amount of titanium atom, based on the weight of the polymer.

The autoclave was purged with hydrogen gas. The temperature of the autoclave was elevated to 160 °C and then, a hydrogenation reaction was conducted under a hydrogen pressure of 35 kg/cm<sup>2</sup>.G for 6 hours.

After completion of the hydrogenation reaction, removal of the solvent was conducted by a conventional method, thereby obtaining a hydrogenated CHD homopolymer.

The degree of hydrogenation of carbon-to-carbon double bonds was 67 mol % as determined by <sup>1</sup>H-NMR.

The number average molecular weight was 21,400.

The  $\overline{M}_w/\overline{M}_n$  ratio was 1.22. The glass transition temperature ( $T_g$ ) was 201 °C as measured in accordance with the DSC method.

Example 24

5 A well dried 4-liter high-pressure autoclave having an electromagnetic induction agitator was purged with dried nitrogen gas by a conventional method.

10 In an atmosphere of dried nitrogen gas, 1,000 g of cyclohexane was charged in the autoclave. The temperature of the cyclohexane was maintained at 70 °C.

15 1,000 g of a 10 wt% cyclohexane solution of the polymer obtained in Example 22 was added to the autoclave. To the resultant polymer solution was added 10 g of a solid catalyst, which comprised 5 wt% of palladium (Pd) supported on barium sulfate ( $\text{BaSO}_4$ ).

20 The autoclave was purged with hydrogen gas. The temperature of the autoclave was elevated to 160 °C and then, a hydrogenation reaction was conducted under a hydrogen pressure of 55 kg/cm<sup>2</sup>.G for 6 hours.

After completion of the hydrogenation reaction, removal of the solvent was conducted by a conventional method, thereby obtaining a hydrogenated CHD homopolymer.

25 The degree of hydrogenation of carbon-to-carbon double bonds was 100 mol % as determined by <sup>1</sup>H-NMR.

The number average molecular weight was 20,800.  
The  $\overline{M}_w/\overline{M}_n$  ratio was 1.24.

The glass transition temperature ( $T_g$ ) was 233 °C  
as measured in accordance with the DSC method.

5     Example 25

A well dried 5-liter high-pressure autoclave  
having an electromagnetic induction agitator was purged  
with dried nitrogen gas by a conventional method.

10     In an atmosphere of dried nitrogen gas, 2,400 g of  
cyclohexane was charged in the autoclave. The tempera-  
ture of the cyclohexane was maintained at room tempera-  
ture.

15     n-BuLi was added to the autoclave in an amount of  
15.0 mmol in terms of the amount of lithium atom. To  
the resultant cyclohexane solution of n-BuLi was added  
7.5 mmol of TMEDA (as a first complexing agent), and  
the resultant mixture was agitated at room temperature  
for 10 minutes.

20     The temperature of the autoclave was elevated to  
40 °C, and then, 11.25 mmol of TMEDA (as a second  
complexing agent) was added to the above-obtained  
mixture.

25     600 g of 1,3-CHD was charged in the autoclave, and  
a polymerization reaction was conducted at 40 °C for 4  
hours. After that period of time, the conversion of

1,3-CHD was 97.4 mol% as measured by gas chromatography.

To the resultant polymerization reaction mixture was added 700 g of cyclohexane to thereby dilute the polymerization reaction mixture. The diluted polymerization reaction mixture was heated to 80 °C, and was transferred by pressure to another 5-liter high-pressure autoclave having an electromagnetic induction agitator, which autoclave had been well dried by a conventional method. Dehydrated n-heptanol was added to the polymerization reaction mixture in an equimolar amount relative to the amount of lithium atoms present in the polymerization reaction mixture, to thereby terminate the polymerization reaction. To the polymerization reaction mixture was added a stabilizing agent [Irganox B215 (0037HX)] manufactured and sold by CIBA GEIGY, Switzerland, and then removal of the solvent was conducted by a conventional method, thereby obtaining a CHD homopolymer.

The number average molecular weight of the obtained polymer was 43,800. The  $\overline{M}_w/\overline{M}_n$  ratio was 1.28.

The 1,2-bond/1,4-bond molar ratio was 58/42. The glass transition temperature ( $T_g$ ) was 167 °C as measured in accordance with the DSC method.

The tensile modulus ( $T_M$ ) of the obtained polymer

was 4,710 MPa (1MPa = 10.20 kg·f/cm<sup>2</sup>).

The heat distortion temperature (HDT, 1.82 MPa) was 131 °C.

Example 26

5           A well dried 5-liter high-pressure autoclave having an electromagnetic induction agitator was purged with dried nitrogen gas by a conventional method.

10           In an atmosphere of dried nitrogen gas, 900 g of cyclohexane was charged in the autoclave. The temperature of the cyclohexane was maintained at room temperature.

15           n-BuLi was added to the autoclave in an amount of 7.5 mmol in terms of the amount of lithium atom. To the resultant cyclohexane solution of n-BuLi was added 3.75 mmol of TMEDA (as a first complexing agent), and the resultant mixture was agitated at room temperature for 10 minutes.

20           The temperature of the autoclave was elevated to 40 °C and then, 5.63 mmol of TMEDA (as a second complexing agent) was added to the above-obtained mixture.

25           600 g of 1,3-CHD was charged in the autoclave, and a polymerization reaction was conducted at 40 °C for 6 hours. After that period of time, the conversion of 1,3-CHD was 94.7 mol% as measured by gas chromatography.

To the resultant polymerization reaction mixture was added 2,000 g of cyclohexane to thereby dilute the polymerization reaction mixture. The diluted polymerization reaction mixture was heated to 80 °C, and was transferred by pressure to another 5-liter high-pressure autoclave having an electromagnetic induction agitator, which autoclave had been well dried by a conventional method. Dehydrated n-heptanol was added to the polymerization reaction mixture in an equimolar amount relative to the amount of lithium atoms present in the polymerization reaction mixture, to thereby terminate the polymerization reaction. To the polymerization reaction mixture was added a stabilizing agent [Irganox B215 (0037HX)] manufactured and sold by CIBA GEIGY, Switzerland, and then removal of the solvent was conducted by a conventional method, thereby obtaining a CHD homopolymer.

The number average molecular weight of the obtained polymer was 81,800. The  $\overline{M}_w/\overline{M}_n$  ratio was 1.32.

The 1,2-bond/1,4-bond molar ratio was 63/37. The glass transition temperature ( $T_g$ ) was 171 °C as measured in accordance with the DSC method.

The tensile modulus (TM) of the obtained polymer was 4,815 MPa (1MPa = 10.20 kg/f/cm<sup>2</sup>).

The heat distortion temperature (HDT, 1.82 MPa)

was 135 °C.

Example 27

5 A well dried 5-liter high-pressure autoclave having an electromagnetic induction agitator was purged with dried nitrogen gas by a conventional method.

In an atmosphere of dried nitrogen gas, 1,500 g of cyclohexane was charged in the autoclave. The temperature of the cyclohexane was maintained at 70 °C.

10 1,500 g of a 10 wt% cyclohexane solution of the polymer obtained in Example 25 was added to the autoclave. To the resultant polymer solution was added a catalyst solution, which was prepared by adding titanocene dichloride (TC) and diisobutyl aluminum hydride (DIBAL-H) to cyclohexane (TC/DIBAL-H molar ratio :  
15 1/6), as a hydrogenation catalyst, in an amount of 290 ppm, in terms of the amount of titanium atom, based on the weight of the polymer.

The autoclave was purged with hydrogen gas. The temperature of the autoclave was elevated to 160 °C and  
20 then, a hydrogenation reaction was conducted under a hydrogen pressure of 35 kg/cm<sup>2</sup>·G for 10 hours.

After completion of the hydrogenation reaction, removal of the solvent was conducted by a conventional method, thereby obtaining a hydrogenated CHD homopolymer.  
25

The degree of hydrogenation of carbon-to-carbon double bonds was 87 mol % as determined by  $^1\text{H-NMR}$ .

The number average molecular weight was 45,300. The  $\overline{M}_w/\overline{M}_n$  ratio was 1.27.

5 The glass transition temperature ( $T_g$ ) was 228 °C as measured in accordance with the DSC method.

The flexural strength (FS) of the obtained polymer was 37.80 MPa (1 MPa = 10.20 kg·f/cm<sup>2</sup>). The flexural modulus (FM) was 6,049 MPa.

10 The heat distortion temperature (HDT, 1.82 MPa) was 188 °C.

#### Example 28

15 A hydrogenation reaction was conducted in substantially the same manner as in Example 27, except that the polymer obtained in Example 26 was used.

After completion of the hydrogenation reaction, removal of the solvent was conducted by a conventional method, thereby obtaining a hydrogenated CHD homopolymer.

20 The degree of hydrogenation of carbon-to-carbon double bonds was 79 mol % as determined by  $^1\text{H-NMR}$ .

The number average molecular weight was 83,600. The  $\overline{M}_w/\overline{M}_n$  ratio was 1.41.

25 The glass transition temperature ( $T_g$ ) was 223 °C as measured in accordance with the DSC method.



The flexural strength (FS) of the obtained polymer was 44.80 MPa (1 MPa = 10.20 kg·f/cm<sup>2</sup>). The flexural modulus (FM) was 6,322 MPa.

5 The heat distortion temperature (HDT, 1.82 MPa) was 190 °C.

Example 29

A well dried 4-liter high-pressure autoclave having an electromagnetic induction agitator was purged with dried nitrogen gas by a conventional method.

10 In an atmosphere of dried nitrogen gas, 1,000 g of cyclohexane was charged in the autoclave. The temperature of the cyclohexane was maintained at 70 °C.

15 1,000 g of a 10 wt% cyclohexane solution of the polymer obtained in Example 25 was added to the autoclave. To the resultant polymer solution was added 10 g of a solid catalyst, which comprised 5 wt% of palladium (Pd) supported on barium sulfate (BaSO<sub>4</sub>).

20 The autoclave was purged with hydrogen gas. The temperature of the autoclave was elevated to 160 °C and then, a hydrogenation reaction was conducted under a hydrogen pressure of 55 kg/cm<sup>2</sup>·G for 6 hours.

25 After completion of the hydrogenation reaction, removal of the solvent was conducted by a conventional method, thereby obtaining a hydrogenated CHD homopolymer.

The degree of hydrogenation of carbon-to-carbon double bonds was 100 mol % as determined by  $^1\text{H}$ -NMR.

The number average molecular weight was 44,100. The  $\overline{M}_w/\overline{M}_n$  ratio was 1.23.

5 The glass transition temperature ( $T_g$ ) was 236 °C as measured in accordance with the DSC method.

The flexural strength (FS) of the obtained polymer was 45.54 MPa (1 MPa = 10.20 kg·f/cm<sup>2</sup>). The flexural modulus (FM) was 6,764 MPa.

10 The heat distortion temperature (HDT, 1.82 MPa) was 192 °C.

#### Example 30

15 A hydrogenation reaction was conducted in substantially the same manner as in Example 29, except that the polymer obtained in Example 26 was used.

After completion of the hydrogenation reaction, removal of the solvent was conducted by a conventional method, thereby obtaining a hydrogenated CHD homopolymer.

20 The degree of hydrogenation of carbon-to-carbon double bonds was 100 mol % as determined by  $^1\text{H}$ -NMR.

The number average molecular weight was 82,700. The  $\overline{M}_w/\overline{M}_n$  ratio was 1.25.

25 The glass transition temperature ( $T_g$ ) was 238 °C as measured in accordance with the DSC method.

The flexural strength (FS) of the obtained polymer was 48.64 MPa (1 MPa = 10.20 kg·f/cm<sup>2</sup>). The flexural modulus (FM) was 7,664 MPa.

5 The heat distortion temperature (HDT, 1.82 MPa) was 198 °C.

Example 31

10 A hydrogenation reaction was conducted in substantially the same manner as in Example 29, except that alumina (Al<sub>2</sub>O<sub>3</sub>) was used as the carrier of the hydrogenation catalyst.

After completion of the hydrogenation reaction, removal of the solvent was conducted by a conventional method, thereby obtaining a hydrogenated CHD homopolymer.

15 The degree of hydrogenation of carbon-to-carbon double bonds was 100 mol % as determined by <sup>1</sup>H-NMR.

The number average molecular weight was 81,900. The  $\overline{M}_w/\overline{M}_n$  ratio was 1.29.

20 The glass transition temperature (T<sub>g</sub>) was 238 °C as measured in accordance with the DSC method.

Example 32

25 A hydrogenation reaction was conducted in substantially the same manner as in Example 29, except that silica (SiO<sub>2</sub>) was used as the carrier of the hydrogenation catalyst.

After completion of the hydrogenation reaction, removal of the solvent was conducted by a conventional method, thereby obtaining a hydrogenated CHD homopolymer.

5        The degree of hydrogenation of carbon-to-carbon double bonds was 100 mol % as determined by  $^1\text{H}$ -NMR.

      The number average molecular weight was 82,100. The  $\overline{M}_w/\overline{M}_n$  ratio was 1.33.

10       The glass transition temperature ( $T_g$ ) was 238 °C as measured in accordance with the DSC method.

Example 33

      A well dried 5-liter high-pressure autoclave having an electromagnetic induction agitator was purged with dried nitrogen gas by a conventional method.

15       In an atmosphere of dried nitrogen gas, 2,400 g of cyclohexane was charged in the autoclave. The temperature of the cyclohexane was maintained at room temperature.

20       n-BuLi was added to the autoclave in an amount of 12.0 mmol in terms of the amount of lithium atom. To the resultant cyclohexane solution of n-BuLi was added 6.0 mmol of TMEDA (as a first complexing agent), and the resultant mixture was agitated at room temperature for 10 minutes.

25       The temperature of the autoclave was elevated to

40 °C and then, 9.0 mmol of TMEDA (as a second complexing agent) was added to the above-obtained mixture.

600 g of 1,3-CHD was charged in the autoclave, and a polymerization reaction was conducted at 40 °C for 6  
5 hours. After that period of time, the conversion of 1,3-CHD was 98.4 mol% as measured by gas chromatography.

To the resultant polymerization reaction mixture was added 700 g of cyclohexane to thereby dilute the  
10 polymerization reaction mixture. The diluted polymerization reaction mixture was heated to 80 °C, and was transferred by pressure to another 5-liter high-pressure autoclave having an electromagnetic induction  
15 agitator, which autoclave had been well dried by a conventional method. Dehydrated n-heptanol was added to the polymerization reaction mixture in an equimolar amount relative to the amount of lithium atoms present in the polymerization reaction mixture, to thereby  
20 terminate the polymerization reaction.

The 1,2-bond/1,4-bond molar ratio of the resultant polymer was 60/40. The glass transition temperature (T<sub>g</sub>) was 170 °C as measured in accordance with the DSC method.

To the resultant polymer solution was added a  
25 catalyst solution, which was prepared by adding

Co(acac)<sub>3</sub> and triisobutyl aluminum (TIBAL) to cyclohexane [Co(acac)<sub>3</sub>/TIBAL molar ratio : 1/6], as a hydrogenation catalyst in an amount of 100 ppm, based on the weight of the polymer.

5        The autoclave was purged with hydrogen gas. The temperature of the autoclave was elevated to 185 °C and then, a hydrogenation reaction was conducted under a hydrogen pressure of 50 kg/cm<sup>2</sup>.G for 4 hours.

10        After completion of the hydrogenation reaction, the autoclave was cooled to room temperature and the pressure in the autoclave was lowered to atmospheric pressure. The autoclave was then purged with nitrogen gas, and TIBAL was treated by adding methanol to the resultant reaction mixture.

15        To the reaction mixture was added a stabilizing agent [Irganox B215 (0037HX)] manufactured and sold by CIBA GEIGY, Switzerland, and then removal of the solvent was conducted by a conventional method, thereby obtaining a hydrogenated CHD homopolymer.

20        The degree of hydrogenation of cyclohexene rings in the CHD homopolymer was 100 mol% as determined by <sup>1</sup>H-NMR. The number average molecular weight of the obtained polymer was 50,700. The  $\overline{M}_w/\overline{M}_n$  ratio was 1.21. The glass transition temperature (T<sub>g</sub>) was 235 °C as  
25        measured in accordance with the DSC method.

The flexural strength (FS) of the obtained polymer was 46.84 MPa (1MPa = 10.20 kg·f/cm<sup>2</sup>) and the flexural modulus (FM) was 6.974 MPa.

5 The heat distortion temperature (HDT, 1.82 MPa) was 195 °C.

Example 34

A well dried 5-liter high-pressure autoclave having an electromagnetic induction agitator was purged with dried nitrogen gas by a conventional method.

10 In an atmosphere of dried nitrogen gas, 2,700 g of cyclohexane was charged in the autoclave. The temperature of the cyclohexane was maintained at room temperature.

15 n-BuLi was added to the autoclave in an amount of 30.0 mmol in terms of the amount of lithium atom. To the resultant cyclohexane solution of n-BuLi was added 15.0 mmol of TMEDA (as a first complexing agent), and the resultant mixture was agitated at room temperature for 10 minutes.

20 The temperature of the autoclave was elevated to 40 °C and then, 22.5 mmol of TMEDA (as a second complexing agent) was added to the above-obtained mixture.

25 In an atmosphere of dried nitrogen gas, 45 g of 1,3-CHD was charged in the autoclave, and a polymerization reaction was conducted at 40 °C for 1 hour.

To the resultant polymerization reaction mixture was added 210 g of isoprene (Ip) in an atmosphere of dried nitrogen gas, and a polymerization reaction was further conducted at 40 °C for 1.5 hours to thereby form a CHD-*Ip* diblock copolymer.

To the resultant polymerization reaction mixture containing the CHD-*Ip* diblock copolymer was added 45 g of 1,3-CHD in an atmosphere of dried nitrogen gas, and a polymerization reaction was further conducted at 40 °C for 3 hours to thereby form a CHD-*Ip*-CHD triblock copolymer.

The resultant polymerization reaction mixture was transferred by pressure to another 5-liter high-pressure autoclave having an electromagnetic induction agitator, which autoclave had been well dried by a conventional method. Dehydrated *n*-heptanol was added to the polymerization reaction mixture in an equimolar amount relative to the amount of lithium atoms present in the polymerization reaction mixture, to thereby terminate the polymerization reaction.

The number average molecular weight of the obtained triblock copolymer was 9,700. The  $\overline{M}_w/\overline{M}_n$  ratio was 1.14.

The 1,2-bond/1,4-bond molar ratio was 48/52.

Example 35



A well dried 5-liter high-pressure autoclave having an electromagnetic induction agitator was purged with dried nitrogen gas by a conventional method.

5 In an atmosphere of dried nitrogen gas, 2,700 g of cyclohexane was charged in the autoclave. The temperature of the cyclohexane was maintained at room temperature.

10 n-BuLi was added to the autoclave in an amount of 37.5 mmol in terms of the amount of lithium atom. To the resultant cyclohexane solution of n-BuLi was added 18.75 mmol of TMEDA (as a first complexing agent), and the resultant mixture was agitated at room temperature for 10 minutes.

15 The temperature of the autoclave was elevated to 40 °C and then, 28.1 mmol of TMEDA (as a second complexing agent) was added to the above-obtained mixture.

20 15 g of isoprene (Ip) was added to the autoclave, followed by the addition of 30 g of 1,3-CHD to the autoclave, and a polymerization reaction was conducted at 40 °C for 1.5 hours to thereby form an Ip-CHD diblock copolymer.

25 To the resultant polymerization reaction mixture containing the Ip-CHD diblock copolymer was added 210 g of Ip, and a polymerization reaction was further conducted at 40 °C for 1.5 hours to thereby form an

Ip-CHD-Ip triblock copolymer.

To the resultant polymerization reaction mixture containing the Ip-CHD-Ip triblock copolymer was added 30 g of 1,3-CHD, and a polymerization reaction was further conducted at 40 °C for 2 hours to thereby form an Ip-CHD-Ip-CHD tetrablock copolymer.

To the resultant polymerization reaction mixture containing the Ip-CHD-Ip-CHD-tetrablock copolymer was added 15 g of Ip, and a polymerization reaction was conducted at 40 °C for 30 minutes to thereby form an Ip-CHD-Ip-CHD-Ip pentablock copolymer.

The resultant polymerization reaction mixture was transferred by pressure to another 5-liter high-pressure autoclave having an electromagnetic induction agitator, which autoclave had been well dried by a conventional method. Dehydrated n-heptanol was added to the polymerization reaction mixture in an equimolar amount relative to the amount of lithium atoms present in the polymerization reaction mixture, to thereby terminate the polymerization reaction.

The number average molecular weight of the obtained pentablock copolymer was 8,200. The  $\overline{M}_w/\overline{M}_n$  ratio was 1.08.

The 1,2-bond/1,4-bond molar ratio was 43/57.

Example 36

A well dried 5-liter high-pressure autoclave having an electromagnetic induction agitator was purged with dried nitrogen gas by a conventional method.

5 In an atmosphere of dried nitrogen gas, 2,700 g of cyclohexane was charged in the autoclave. The temperature of the cyclohexane was maintained at room temperature.

10 n-BuLi was added to the autoclave in an amount of 30.0 mmol in terms of the amount of lithium atom. To the resultant cyclohexane solution of n-BuLi was added 15.0 mmol of TMEDA (as a first complexing agent), and the resultant mixture was agitated at room temperature for 10 minutes.

15 The temperature of the autoclave was elevated to 40 °C and then, 22.5 mmol of TMEDA (as a second complexing agent) was added to the above-obtained mixture.

15 g of 1,3-CHD was charged in the autoclave, and a polymerization reaction was conducted at 40 °C for 1 hour.

20 To the resultant polymerization reaction mixture was added 270 g of isoprene (Ip), and a polymerization reaction was further conducted at 40 °C for 2 hours to thereby form a CHD-Ip diblock copolymer.

25 To the resultant polymerization reaction mixture containing the CHD-Ip diblock copolymer was added 15 g

of 1,3-CHD, and a polymerization reaction was further conducted at 40 °C for 3 hours to thereby form a CHD-IP-CHD triblock copolymer.

5 The resultant polymerization reaction mixture was transferred by pressure to another 5-liter high-pressure autoclave having an electromagnetic induction agitator, which autoclave had been well dried by a conventional method. Dehydrated n-heptanol was added to the polymerization reaction mixture in an equimolar  
10 amount relative to the amount of lithium atoms present in the polymerization reaction mixture, to thereby terminate the polymerization reaction.

The number average molecular weight of the obtained triblock copolymer was 10,500. The  $\overline{M}_w/\overline{M}_n$  ratio  
15 was 1.04.

The 1,2-bond/1,4-bond molar ratio was 45/55.

#### Example 37

A well dried 5-liter high-pressure autoclave having an electromagnetic induction agitator was purged  
20 with dried nitrogen gas by a conventional method.

In an atmosphere of dried nitrogen gas, 1,500 g of cyclohexane was charged in the autoclave. The temperature of the cyclohexane was maintained at 70 °C.

25 1,500 g of a 10 wt% cyclohexane solution of the polymer obtained in Example 36 was added to the auto-

clave. To the resultant polymer solution was added a catalyst solution, which was prepared by adding titanocene dichloride (TC) and diisobutyl aluminum hydride (DIBAL-H) to cyclohexane (TC/DIBAL-H molar ratio :  
5 1/6), as a hydrogenation catalyst, in an amount of 100 ppm, in terms of the amount of titanium atom, based on the weight of the polymer.

The autoclave was purged with hydrogen gas. The temperature of the autoclave was elevated to 100 °C and  
10 then, a hydrogenation reaction was conducted under a hydrogen pressure of 8 kg/cm<sup>2</sup>·G for 1 hour, thereby obtaining a hydrogenated CHD-Ip-CHD triblock copolymer.

The degree of hydrogenation of the isoprene (Ip) polymer block of the polymer was 100 mol % as determined by <sup>1</sup>H-NMR. The CHD polymer block was not hydrogenated.  
15

#### Example 38

A well dried 5-liter high-pressure autoclave having an electromagnetic induction agitator was purged  
20 with dried nitrogen gas by a conventional method.

In an atmosphere of dried nitrogen gas, 2,400 g of cyclohexane was charged in the autoclave. The temperature of the cyclohexane was maintained at room temperature.

25 n-BuLi was added to the autoclave in an amount of

15.0 mmol in terms of the amount of lithium atom. To the resultant cyclohexane solution of n-BuLi was added 7.5 mmol of TMEDA (as a first complexing agent), and the resultant mixture was agitated at room temperature for 10 minutes.

The temperature of the autoclave was elevated to 40 °C and then, 11.25 mmol of TMEDA (as a second complexing agent) was added to the above-obtained mixture.

300 g of 1,3-CHD was charged in the autoclave, and a polymerization reaction was conducted at 40 °C for 20 minutes. After that period of time, the conversion of 1,3-CHD was 47.8 mol% as measured by gas chromatography.

Subsequently, 300 g of isoprene (Ip) was charged in the autoclave, and a polymerization reaction was further conducted at 40 °C for 5 hours.

Upon addition of Ip to the polymerization reaction system of 1,3-CHD, interruption of the polymerization reaction of 1,3-CHD occurred because a polymerization reaction of Ip proceeded in preference to a polymerization reaction of 1,3-CHD. Upon consumption of nearly all of the Ip monomers added, a polymerization reaction of 1,3-CHD started again. As a result, a CHD-*Ip*-CHD triblock copolymer was obtained.

The resultant polymerization reaction mixture was transferred by pressure to another 5-liter high-pressure autoclave having an electromagnetic induction agitator, which autoclave had been well dried by a conventional method. Dehydrated n-heptanol was added to the polymerization reaction mixture in an equimolar amount relative to the amount of lithium atoms present in the polymerization reaction mixture, to thereby terminate the polymerization reaction.

The number average molecular weight of the obtained triblock copolymer was 41,500. The  $\overline{M}_w/\overline{M}_n$  ratio was 1.31. The 1,2-bond/1,4-bond molar ratio was 49/51. The glass transition temperature ( $T_g$ ) of the CHD polymer block of the copolymer was 152 °C as measured in accordance with the DSC method.

The tensile strength (TS) of the obtained triblock copolymer was 26.2 MPa (1MPa = 10.20 kg·f/cm<sup>2</sup>). The tensile elongation (TE) was 157 %. The flexural strength (FS) was 23.0 MPa and the flexural modulus (FM) was 2,950 MPa.

The Izod impact strength was N.B. (no break).

Example 39

A well dried 5-liter high-pressure autoclave having an electromagnetic induction agitator was purged with dried nitrogen gas by a conventional method.

5 In an atmosphere of dried nitrogen gas, 1,800 g of cyclohexane was charged in the autoclave. The temperature of the cyclohexane was maintained at room temperature.

10 n-BuLi was added to the autoclave in an amount of 10.0 mmol in terms of the amount of lithium atom. To the resultant cyclohexane solution of n-BuLi was added 5.0 mmol of TMEDA (as a first complexing agent), and the resultant mixture was agitated at room temperature for 10 minutes.

15 The temperature of the autoclave was elevated to 40 °C and then, 7.5 mmol of TMEDA (as a second complexing agent) was added to the above-obtained mixture.

20 200 g of 1,3-CHD was charged in the autoclave, and a polymerization reaction was conducted at 40 °C for 20 minutes. After that period of time, the conversion of 1,3-CHD was 49.5 mol% as measured by gas chromatography.

25 Subsequently, 400 g of isoprene (Ip) was charged in the autoclave, and a polymerization reaction was further conducted at 40 °C for 6 hours.



Upon addition of Ip to the polymerization reaction system of 1,3-CHD, interruption of the polymerization reaction of 1,3-CHD occurred because a polymerization reaction of Ip proceeded in preference to a polymerization reaction of 1,3-CHD. Upon consumption of nearly all of the Ip monomers added, a polymerization reaction of 1,3-CHD started again. As a result, a CHD-*Ip*-CHD triblock copolymer was obtained.

The resultant polymerization reaction mixture was diluted with 1000 g of cyclohexane, and heated to 70 °C. The diluted polymerization reaction mixture was transferred by pressure to another 5-liter high-pressure autoclave having an electromagnetic induction agitator, which autoclave had been well dried by a conventional method. Dehydrated *n*-heptanol was added to the polymerization reaction mixture in an equimolar amount relative to the amount of lithium atoms present in the polymerization reaction mixture, to thereby terminate the polymerization reaction.

The number average molecular weight of the obtained triblock copolymer was 62,000. The  $\overline{M}_w/\overline{M}_n$  ratio was 1.44. The 1,2-bond/1,4-bond molar ratio was 48/52. The glass transition temperature (*T<sub>g</sub>*) of the CHD polymer block of the copolymer was 151 °C as measured in accordance with the DSC method.

The tensile strength (TS) of the obtained triblock copolymer was 19.5 MPa (1MPa = 10.20 kg·f/cm<sup>2</sup>). The tensile elongation (TE) was 695 %.

Example 40

5        A well dried 5-liter high-pressure autoclave having an electromagnetic induction agitator was purged with dried nitrogen gas by a conventional method.

10       In an atmosphere of dried nitrogen gas, 2,400 g of cyclohexane was charged in the autoclave. The temperature of the cyclohexane was maintained at room temperature.

15       n-BuLi was added to the autoclave in an amount of 15.0 mmol in terms of the amount of lithium atom. To the resultant cyclohexane solution of n-BuLi was added 7.5 mmol of TMEDA (as a first complexing agent), and the resultant mixture was agitated at room temperature for 10 minutes.

20       The temperature of the autoclave was elevated to 40 °C and then, 11.25 mmol of TMEDA (as a second complexing agent) was added to the above-obtained mixture.

25       300 g of 1,3-CHD was mixed with 300 g of Ip. The resultant mixture was charged in the autoclave, and a polymerization reaction was conducted at 40 °C for 6 hours.

In the polymerization reaction system in which 1,3-CHD and Ip coexisted, a polymerization reaction of Ip proceeded in preference to a polymerization reaction of 1,3-CHD. Upon consumption of nearly all of the Ip monomers present, a polymerization reaction of 1,3-CHD started. The conversion of 1,3-CHD was 98.3 mol% as measured by gas chromatography. As a result, an Ip-CHD diblock copolymer was obtained.

The resultant polymerization reaction mixture was heated to 70 °C, and transferred by pressure to another 5-liter high-pressure autoclave having an electromagnetic induction agitator, which autoclave had been well dried by a conventional method. Dehydrated n-heptanol was added to the polymerization reaction mixture in an equimolar amount relative to the amount of lithium atoms present in the polymerization reaction mixture, to thereby terminate the polymerization reaction.

The number average molecular weight of the obtained diblock copolymer was 40,100. The  $\overline{M}_w/\overline{M}_n$  ratio was 1.49. The 1,2-bond/1,4-bond molar ratio was 51/49. The glass transition temperature ( $T_g$ ) of the CHD polymer block of the copolymer was 153 °C as measured in accordance with the DSC method.

The tensile strength (TS) of the obtained diblock copolymer was 12.5 MPa (1MPa = 10.20 kg·f/cm<sup>2</sup>). The

tensile elongation (TE) was 28 %. The flexural strength (FS) was 18.7 MPa and the flexural modulus (FM) was 815 MPa.

The Izod impact strength was N.B. (no break).

5     Example 41

10     A polymerization reaction was conducted in substantially the same manner as in Example 38, except that a monomer mixture of 480 g of 1,3-CHD and 120 g of Ip was used. After 6 hours of the polymerization reaction, the conversion of 1,3-CHD was 96.6 mol% as measured by gas chromatography.

15     Because the polymerization reaction system contained 1,3-CHD in a large amount, as compared to Ip, a polymerization reaction of 1,3-CHD also started at an early stage of the polymerization reaction of Ip, although the polymerization reaction of Ip proceeded in preference to the polymerization reaction of 1,3-CHD. As a result, a copolymer containing portions in which Ip and 1,3-CHD are randomly copolymerized was obtained.

20     The resultant polymerization reaction mixture was heated to 70 °C, and transferred by pressure to another 5-liter high-pressure autoclave having an electromagnetic induction agitator, which autoclave had been well dried by a conventional method. Dehydrated n-heptanol  
25     was added to the polymerization reaction mixture in an

equimolar amount relative to the amount of lithium atoms present in the polymerization reaction mixture, to thereby terminate the polymerization reaction.

5 The number average molecular weight of the obtained copolymer was 41,200. The  $\overline{M}_w/\overline{M}_n$  ratio was 1.41. The 1,2-bond/1,4-bond molar ratio was 52/48. The glass transition temperature ( $T_g$ ) of the CHD polymer block of the copolymer was 154 °C as measured in accordance with the DSC method.

10 The tensile strength (TS) of the obtained copolymer was 47.5 MPa (1MPa = 10.20 kg·f/cm<sup>2</sup>). The tensile elongation (TE) was 5 %. The flexural strength (FS) was 92.9 MPa and the flexural modulus (FM) was 3,210 MPa.

15 The heat distortion temperature (HDT, 1.82 MPa) was 128 °C.

The Izod impact strength was 78.2 J/m.

#### Example 42

20 A well dried 5-liter high-pressure autoclave having an electromagnetic induction agitator was purged with dried nitrogen gas by a conventional method.

In an atmosphere of dried nitrogen gas, 1,500 g of cyclohexane was charged in the autoclave. The temperature of the cyclohexane was maintained at 70 °C.

25 1,500 g of a 10 wt% cyclohexane solution of the

polymer obtained in Example 38 was added to the autoclave. To the resultant polymer solution was added a catalyst solution, which was prepared by adding titanocene dichloride (TC) and diisobutyl aluminum hydride (DIBAL-H) to cyclohexane (TC/DIBAL-H molar ratio : 1/6), as a hydrogenation catalyst, in an amount of 290 ppm, in terms of the amount of titanium atom, based on the weight of the polymer.

The autoclave was purged with hydrogen gas. The temperature of the autoclave was elevated to 160 °C and then, a hydrogenation reaction was conducted under a hydrogen pressure of 35 kg/cm<sup>2</sup>.G for 6 hours.

After completion of the hydrogenation reaction, removal of the solvent was conducted by a conventional method, thereby obtaining a hydrogenated CHD-Ip-CHD triblock copolymer.

The degree of hydrogenation of the isoprene (Ip) polymer block was 100 % and that of the CHD polymer block was 96 %, as determined by <sup>1</sup>H-NMR.

The number average molecular weight was 42,400. The  $\overline{M_w}/\overline{M_n}$  ratio was 1.28. The glass transition temperature (T<sub>g</sub>) of the hydrogenated CHD polymer block of the copolymer was 233 °C as measured in accordance with the DSC method.

The tensile strength (TS) of the obtained triblock

copolymer was 30.8 MPa (1MPa = 10.20 kg·f/cm<sup>2</sup>). The tensile elongation (TE) was 357 %. The flexural strength (FS) was 29.0 MPa and the flexural modulus (FM) was 3,050 MPa.

5           The Izod impact strength was N.B. (no break).

Example 43

A hydrogenation reaction was conducted in substantially the same manner as in Example 42, except that the polymer obtained in Example 39 was used.

10           After completion of the hydrogenation reaction, removal of the solvent was conducted by a conventional method, thereby obtaining a hydrogenated CHD-Ip-CHD triblock copolymer.

15           The degree of hydrogenation of the isoprene (Ip) polymer block was 100 % and that of the CHD polymer block was 92 %, as determined by <sup>1</sup>H-NMR.

20           The number average molecular weight was 62,700. The  $\overline{M}_w/\overline{M}_n$  ratio was 1.39. The glass transition temperature (T<sub>g</sub>) of the hydrogenated CHD polymer block of the copolymer was 232 °C as measured in accordance with the DSC method.

25           The tensile strength (TS) of the obtained triblock copolymer was 24.3 MPa (1MPa = 10.20 kg·f/cm<sup>2</sup>). The tensile elongation (TE) was 706 %.

Example 44

A well dried 4-liter high-pressure autoclave having an electromagnetic induction agitator was purged with dried nitrogen gas by a conventional method.

5 In an atmosphere of dried nitrogen gas, 1,000 g of cyclohexane was charged in the autoclave. The temperature of the cyclohexane was maintained at 70 °C.

1,000 g of a 10 wt% cyclohexane solution of the polymer obtained in Example 38 was added to the autoclave. To the resultant polymer solution was added  
10 10 g of a solid catalyst, which comprised 5 wt% of palladium (Pd) supported by barium sulfate ( $\text{BaSO}_4$ ).

The autoclave was purged with hydrogen gas. The temperature of the autoclave was elevated to 160 °C and then, a hydrogenation reaction was conducted under a  
15 hydrogen pressure of 55 kg/cm<sup>2</sup>.G for 6 hours.

After completion of the hydrogenation reaction, removal of the solvent was conducted by a conventional method, thereby obtaining a hydrogenated CHD-*Ip*-CHD triblock copolymer.

20 With respect to both of the isoprene (*Ip*) polymer block and the CHD polymer block, the degree of hydrogenation was 100 %, as determined by <sup>1</sup>H-NMR.

The number average molecular weight was 40,900. The  $\overline{M}_w/\overline{M}_n$  ratio was 1.33. The glass transition  
25 temperature (*T<sub>g</sub>*) of the hydrogenated CHD polymer block



of the copolymer was 232 °C as measured in accordance with the DSC method.

The tensile strength (TS) of the obtained triblock copolymer was 30.2 MPa (1MPa = 10.20 kg·f/cm<sup>2</sup>). The tensile elongation (TE) was 320 %. The flexural strength (FS) was 28.2 MPa and the flexural modulus (FM) was 3,150 MPa.

The Izod impact strength was N.B. (no break).

#### Example 45

A hydrogenation reaction was conducted in substantially the same manner as in Example 44, except that the polymer obtained in Example 39 was used.

After completion of the hydrogenation reaction, removal of the solvent was conducted by a conventional method, thereby obtaining a hydrogenated CHD-Ip-CHD triblock copolymer.

With respect to both of the isoprene (Ip) polymer block and the CHD polymer block, the degree of hydrogenation was 100 %, as determined by <sup>1</sup>H-NMR.

The number average molecular weight was 61,900. The  $\overline{M}_w/\overline{M}_n$  ratio was 1.46. The glass transition temperature (T<sub>g</sub>) of the hydrogenated CHD polymer block of the copolymer was 230 °C as measured in accordance with the DSC method.

The tensile strength (TS) of the obtained triblock

copolymer was 25.9 MPa (1MPa = 10.20 kg·f/cm<sup>2</sup>). The tensile elongation (TE) was 650 %.

Example 46

5 A well dried 5-liter high-pressure autoclave having an electromagnetic induction agitator was purged with dried nitrogen gas by a conventional method.

10 In an atmosphere of dried nitrogen gas, 2,400 g of cyclohexane was charged in the autoclave. The temperature of the cyclohexane was maintained at room temperature.

15 n-BuLi was added to the autoclave in an amount of 15.0 mmol in terms of the amount of lithium atom. To the resultant cyclohexane solution of n-BuLi was added 7.5 mmol of TMEDA (as a first complexing agent), and the resultant mixture was agitated at room temperature for 10 minutes.

20 The temperature of the autoclave was elevated to 40 °C and then, 11.25 mmol of TMEDA (as a second complexing agent) was added to the above-obtained mixture.

25 300 g of 1,3-CHD was charged in the autoclave, and a polymerization reaction was conducted at 40 °C for 20 minutes. After that period of time, the conversion of 1,3-CHD was 50.1 mol% as measured by gas chromatography.

Subsequently, 300 g of styrene (St) was charged in the autoclave, and a polymerization reaction was further conducted at 40 °C for 5 hours.

5        Upon addition of St to the polymerization reaction system of 1,3-CHD, interruption of the polymerization reaction of 1,3-CHD occurred because a polymerization reaction of St proceeded in preference to a polymerization reaction of 1,3-CHD. Upon consumption of nearly all of the St monomers added, a polymerization reaction  
10       of 1,3-CHD started again. As a result, a CHD-St-CHD triblock copolymer was obtained.

      The resultant polymerization reaction mixture was transferred by pressure to another 5-liter high-pressure autoclave having an electromagnetic induction  
15       agitator, which autoclave had been well dried by a conventional method. Dehydrated n-heptanol was added to the polymerization reaction mixture in an equimolar amount relative to the amount of lithium atoms present in the polymerization reaction mixture, to thereby  
20       terminate the polymerization reaction.

      The number average molecular weight of the obtained triblock copolymer was 40,600. The  $\overline{M}_w/\overline{M}_n$  ratio was 1.21. The 1,2-bond/1,4-bond molar ratio was 56/44. The glass transition temperature ( $T_g$ ) of the CHD polymer block of the copolymer was 162 °C as measured in  
25

accordance with the DSC method.

The flexural strength (FS) of the obtained tri-block copolymer was 33.5 MPa (1 MPa = 10.20 kg·f/cm<sup>2</sup>) and the flexural modulus (FM) was 2,980 MPa.

5        The heat distortion temperature (HDT, 1.82MPa) was 88 °C.

Example 47

10        A well dried 5-liter high-pressure autoclave having an electromagnetic induction agitator was purged with dried nitrogen gas by a conventional method.

In an atmosphere of dried nitrogen gas, 2,400 g of cyclohexane was charged in the autoclave. The temperature of the cyclohexane was maintained at room temperature.

15        n-BuLi was added to the autoclave in an amount of 10.0 mmol in terms of the amount of lithium atom. To the resultant cyclohexane solution of n-BuLi was added 5.0 mmol of TMEDA (as a first complexing agent), and the resultant mixture was agitated at room temperature  
20        for 10 minutes.

The temperature of the autoclave was elevated to 40 °C and then, 7.5 mmol of TMEDA (as a second complexing agent) was added to the above-obtained mixture.

25        100 g of 1,3-CHD was charged in the autoclave, and

a polymerization reaction was conducted at 40 °C for 2 hours, to thereby obtain a CHD homopolymer (polymer 1).

Subsequently, 400 g of styrene (St) was charged in the autoclave, and a polymerization reaction was further conducted at 40 °C for 3 hours, to thereby obtain a CHD-St diblock copolymer (polymer 2).

In addition, 100 g of 1,3-CHD was charged in the autoclave, and a polymerization reaction was further conducted at 40 °C for 5 hours, to thereby obtain a CHD-St-CHD triblock copolymer (polymer 3).

The resultant polymerization reaction mixture was heated to 70 °C, and transferred by pressure to another 5-liter high-pressure autoclave having an electromagnetic induction agitator, which autoclave had been well dried by a conventional method. Dehydrated n-heptanol was added to the polymerization reaction mixture in an equimolar amount relative to the amount of lithium atoms present in the polymerization reaction mixture, to thereby terminate the polymerization reaction.

The respective number average molecular weights of the obtained polymers 1, 2 and 3 were 10,300, 49,800 and 60,700. The respective  $\overline{M}_w/\overline{M}_n$  ratios were 1.04, 1.10 and 1.25. The 1,2-bond/1,4-bond molar ratio of the polymer 3 was 53/47. The glass transition temperature ( $T_g$ ) of the CHD polymer block of the polymer 3 was

156 °C as measured in accordance with the DSC method.

The tensile strength (TS) of the obtained polymer 3 was 18.9 MPa (1MPa = 10.20 kg·f/cm<sup>2</sup>). The tensile elongation (TE) was 2 %. The flexural strength (FS) was 46.2 MPa and the flexural modulus (FM) was 3,232 MPa.

The heat distortion temperature (HDT, 1.82 MPa) of the polymer 3 was 78 °C.

#### Example 48

10 A well dried 5-liter high-pressure autoclave having an electromagnetic induction agitator was purged with dried nitrogen gas by a conventional method.

In an atmosphere of dried nitrogen gas, 2,400 g of cyclohexane was charged in the autoclave. The temperature of the cyclohexane was maintained at room temperature.

15 n-BuLi was added to the autoclave in an amount of 15.0 mmol in terms of the amount of lithium atom. To the resultant cyclohexane solution of n-BuLi was added 20 7.5 mmol of TMEDA (as a first complexing agent), and the resultant mixture was agitated at room temperature for 10 minutes.

The temperature of the autoclave was elevated to 40 °C, and then, 11.25 mmol of TMEDA (as a second complexing agent) was added to the above-obtained

mixture.

300 g of 1,3-CHD was mixed with 300 g of St. The resultant mixture was charged in the autoclave, and a polymerization reaction was conducted at 40 °C for 6 hours.

In the polymerization reaction system in which 1,3-CHD and St coexisted, a polymerization reaction of St proceeded in preference to a polymerization reaction of 1,3-CHD. Upon consumption of nearly all of the St monomers present, a polymerization reaction of 1,3-CHD started. The conversion of 1,3-CHD was 98.3 mol% as measured by gas chromatography. As a result, a St-CHD diblock copolymer was obtained.

The resultant polymerization reaction mixture was heated to 70 °C, and transferred by pressure to another 5-liter high-pressure autoclave having an electromagnetic induction agitator, which autoclave had been well dried by a conventional method. Dehydrated n-heptanol was added to the polymerization reaction mixture in an equimolar amount relative to the amount of lithium atoms present in the polymerization reaction mixture, to thereby terminate the polymerization reaction.

The number average molecular weight of the obtained diblock copolymer was 40,080. The  $\overline{M}_w/\overline{M}_n$  ratio was 1.23. The 1,2-bond/1,4-bond molar ratio was 57/43.

The glass transition temperature ( $T_g$ ) of the CHD polymer block of the copolymer was 161 °C as measured in accordance with the DSC method.

5 The flexural strength (FS) of the obtained diblock copolymer was 18.5 MPa (1 MPa = 10.20 kg·f/cm<sup>2</sup>) and the flexural modulus (FM) was 5,430 MPa.

The heat distortion temperature (HDT, 1.82 MPa) was 72 °C.

Example 49

10 A well dried 5-liter high-pressure autoclave having an electromagnetic induction agitator was purged with dried nitrogen gas by a conventional method.

15 In an atmosphere of dried nitrogen gas, 2,400 g of cyclohexane was charged in the autoclave. The temperature of the cyclohexane was maintained at room temperature.

20 n-BuLi was added to the autoclave in an amount of 15.0 mmol in terms of the amount of lithium atom. To the resultant cyclohexane solution of n-BuLi was added 7.5 mmol of TMEDA (as a first complexing agent), and the resultant mixture was agitated at room temperature for 10 minutes.

25 The temperature of the autoclave was elevated to 40 °C and then, 11.25 mmol of TMEDA (as a second complexing agent) was added to the above-obtained



mixture.

200 g of 1,3-CHD, 200 g of Ip and 200 g of St were mixed together. The resultant mixture was charged in the autoclave, and a polymerization reaction was conducted at 40 °C for 6 hours.

In the polymerization reaction system in which 1,3-CHD, Ip and St coexisted, a polymerization reaction of St proceeded in preference to a polymerization reaction of 1,3-CHD and a polymerization reaction of Ip. Upon consumption of nearly all of the St monomers present, a polymerization reaction of Ip started, because a polymerization reaction of Ip proceeded in preference to a polymerization reaction of 1,3-CHD. Upon consumption of nearly all of the Ip monomers present; a polymerization reaction of 1,3-CHD started. The conversion of 1,3-CHD was 99.5 mol% as measured by gas chromatography. As a result, a St-IP-CHD triblock copolymer was obtained.

The resultant polymerization reaction mixture was heated to 70 °C, and transferred by pressure to another 5-liter high-pressure autoclave having an electromagnetic induction agitator, which autoclave had been well dried by a conventional method. Dehydrated n-heptanol was added to the polymerization reaction mixture in an equimolar amount relative to the amount of lithium

atoms present in the polymerization reaction mixture, to thereby terminate the polymerization reaction.

The number average molecular weight of the obtained triblock copolymer was 40,200. The  $\overline{M}_w/\overline{M}_n$  ratio was 1.21. The 1,2-bond/1,4-bond molar ratio was 53/47. The glass transition temperature ( $T_g$ ) of the CHD polymer block of the copolymer was 156 °C as measured in accordance with the DSC method.

The tensile strength (TS) of the obtained triblock copolymer was 22.4 MPa (1MPa = 10.20 kg·f/cm<sup>2</sup>). The tensile elongation (TE) was 4 %. The flexural strength (FS) was 45.0 MPa and the flexural modulus (FM) was 1,470 MPa.

#### Example 50

A well dried 5-liter high-pressure autoclave having an electromagnetic induction agitator was purged with dried nitrogen gas by a conventional method.

In an atmosphere of dried nitrogen gas, 1,500 g of cyclohexane was charged in the autoclave. The temperature of the cyclohexane was maintained at 70 °C.

1,500 g of a 10 wt% cyclohexane solution of the polymer obtained in Example 46 was added to the autoclave. To the resultant polymer solution was added a catalyst solution, which was prepared by adding titanocene dichloride (TC) and diisobutyl aluminum hydride

(DIBAL-H) to cyclohexane (TC/DIBAL-H molar ratio : 1/6), as a hydrogenation catalyst, in an amount of 290 ppm, in terms of the amount of titanium atom, based on the weight of the polymer.

5           The autoclave was purged with hydrogen gas. The temperature of the autoclave was elevated to 160 °C and then, a hydrogenation reaction was conducted under a hydrogen pressure of 35 kg/cm<sup>2</sup>·G for 10 hours.

10           After completion of the hydrogenation reaction, removal of the solvent was conducted by a conventional method, thereby obtaining a hydrogenated CHD-St-CHD triblock copolymer.

15           The degree of hydrogenation of the CHD polymer block of the copolymer was 96 mol % as determined by <sup>1</sup>H-NMR. The St polymer block was not hydrogenated.

          The number average molecular weight was 40,400. The  $\overline{M}_w/\overline{M}_n$  ratio was 1.20. The glass transition temperature (T<sub>g</sub>) of the CHD polymer block was 232 °C as measured in accordance with the DSC method.

20           The flexural strength (FS) of the copolymer was 38.8 MPa (1 MPa = 10.20 kg·f/cm<sup>2</sup>), and the flexural modulus (FM) was 4,060 MPa.

          The heat distortion temperature (HDT, 1.82 MPa) was 90 °C.

25           Example 51

A hydrogenation reaction was conducted in substantially the same manner as in Example 50, except that the polymer obtained in Example 48 was used.

After completion of the hydrogenation reaction,  
5 removal of the solvent was conducted by a conventional method, thereby obtaining a hydrogenated St-CHD di-block copolymer.

The degree of hydrogenation of the CHD polymer block was 96 mol % as determined by  $^1\text{H-NMR}$ . The St  
10 polymer block was not hydrogenated.

The number average molecular weight was 40,400. The  $\overline{M}_w/\overline{M}_n$  ratio was 1.19. The glass transition temperature ( $T_g$ ) of the CHD polymer block was 234 °C as measured in accordance with the DSC method.

15 The flexural strength (FS) of the copolymer was 22.8 MPa (1 MPa = 10.20 kg·f/cm<sup>2</sup>) and the flexural modulus (FM) was 5,810 MPa.

The heat distortion temperature (HDT, 1.82 MPa) was 82 °C.

20 Example 52

A well dried 4-liter high-pressure autoclave having an electromagnetic induction agitator was purged with dried nitrogen gas by a conventional method.

25 In an atmosphere of dried nitrogen gas, 1,000 g of cyclohexane was charged in the autoclave. The tempera-

ture of the cyclohexane was maintained at 70 °C.

1,000 g of a 10 wt% cyclohexane solution of the polymer obtained in Example 46 was added to the autoclave. To the resultant polymer solution was added 50  
5 g of a solid catalyst, which comprised 5 wt% of palladium (Pd) supported by barium sulfate ( $\text{BaSO}_4$ ).

The autoclave was purged with hydrogen gas. The temperature of the autoclave was elevated to 160 °C and then, a hydrogenation reaction was conducted under a  
10 hydrogen pressure of 55 kg/cm<sup>2</sup>.G for 6 hours.

After completion of the hydrogenation reaction, removal of the solvent was conducted by a conventional method, thereby obtaining a hydrogenated CHD-St-CHD triblock copolymer.

15 With respect to both of the CHD polymer block and St polymer block, the degree of hydrogenation was 100 mol % as determined by <sup>1</sup>H-NMR.

The number average molecular weight was 41,600. The  $\overline{M}_w/\overline{M}_n$  ratio was 1.29. The respective glass  
20 transition temperatures ( $T_g$ ) of the hydrogenated CHD polymer block and hydrogenated styrene polymer block were 232 °C and 147 °C, as measured in accordance with the DSC method.

The flexural strength (FS) of the copolymer was  
25 42.8 MPa (1 MPa = 10.20 kg·f/cm<sup>2</sup>) and the flexural

modulus (FM) was 5,025 MPa.

The heat distortion temperature (HDT, 1.82 MPa) was 129 °C.

Example 53

5 A hydrogenation reaction was conducted in substantially the same manner as in Example 52, except that the polymer obtained in Example 48 was used.

After completion of the hydrogenation reaction, removal of the solvent was conducted by a conventional method, thereby obtaining a hydrogenated St-CHD di-  
10 block copolymer.

With respect to both of the CHD polymer block and St polymer block, the degree of hydrogenation was 100 mol % as determined by  $^1\text{H-NMR}$ .

15 The number average molecular weight was 41,000. The  $\overline{M}_w/\overline{M}_n$  ratio was 1.26. The respective glass transition temperatures ( $T_g$ ) of the hydrogenated CHD polymer block and hydrogenated styrene polymer block were 229 °C and 149 °C, as measured in accordance with  
20 the DSC method.

The flexural strength (FS) of the copolymer was 28.1 MPa (1 MPa = 10.20 kg·f/cm<sup>2</sup>), and the flexural modulus (FM) was 6,100 MPa.

25 The heat distortion temperature (HDT, 1.82 MPa) was 128 °C.

Example 54

A well dried 100 ml Schlenk tube was purged with dried argon gas by a conventional method. 1 g of the polymer obtained in Example 46 and 50 ml of trichlorobenzene were charged in the Schlenk tube. In an atmosphere of dried argon gas, the resultant mixture was heated to 140 °C under agitation, thereby dissolving the polymer in the trichlorobenzene.

To the resultant polymer solution was added tetrachloro-1,4-benzoquinone (p-chloranil) in an amount of 4 equivalents per equivalent of hexene units in the polymer. A dehydrogenation reaction was conducted at 140 °C for 20 hours. After completion of the reaction, removal of the solvent was conducted by a conventional method, thereby obtaining a light yellow dehydrogenated polymer. The UV spectrum of the obtained dehydrogenated polymer was measured. It was confirmed that, in the dehydrogenated cyclic conjugated diene polymer, 76 % of the cyclohexene units in the polymer obtained in Example 46 had been converted to benzene rings.

Example 55

A well dried 100 ml Schlenk tube was purged with dried argon gas by a conventional method. 1 g of the polymer obtained in Example 48 and 50 ml of trichlorobenzene were charged in the Schlenk tube. In an atmos-

phere of dried argon gas, the resultant mixture was heated to 140 °C under agitation, thereby dissolving the polymer in the trichlorobenzene.

To the resultant polymer solution was added tetra-  
5 chloro-1,4-benzoquinone (p-chloranil) in an amount of 4 equivalents per equivalent of cyclohexene units in the polymer. A dehydrogenation reaction was conducted at 140 °C for 20 hours. After completion of the reaction, removal of the solvent was conducted by a conventional  
10 method, thereby obtaining a light yellow dehydrogenated polymer. The UV spectrum of the obtained dehydrogenated polymer was measured. It was confirmed that, in the dehydrogenated cyclic conjugated diene polymer, 82 % of the cyclohexene units in the polymer obtained in Exam-  
15 ple 48 had been converted to benzene rings.

Example 56

A well dried 5-liter high-pressure autoclave having an electromagnetic induction agitator was purged with dried nitrogen gas by a conventional method.

20 In an atmosphere of dried nitrogen gas, 2,700 g of cyclohexane was charged in the autoclave. The temperature of the cyclohexane was maintained at room temperature.

25 n-BuLi was added to the autoclave in an amount of 30.0 mmol in terms of the amount of lithium atom. To



the resultant cyclohexane solution of n-BuLi was added 15.0 mmol of TMEDA (as a first complexing agent), and the resultant mixture was agitated at room temperature for 10 minutes.

5           The temperature of the autoclave was elevated to 40 °C and then, 22.5 mmol of TMEDA (as a second complexing agent) was added to the above-obtained mixture.

10           45 g of 1,3-CHD was charged in the autoclave, and a polymerization reaction was conducted at 40 °C for 1 hour.

15           Subsequently, 700 g of a 30 wt% solution of butadiene (Bd) in cyclohexane (Bd 210 g) was charged in the autoclave, and a polymerization reaction was further conducted at 40 °C for 1 hour, to thereby form a CHD-Bd diblock copolymer.

20           To the resultant polymerization reaction mixture containing the CHD-Bd diblock copolymer was added 45 g of 1,3-CHD, and a polymerization reaction was further conducted at 40 °C for 3 hours, to thereby form a CHD-Bd-CHD triblock copolymer.

25           The resultant polymerization reaction mixture was transferred by pressure to another 5-liter high-pressure autoclave having an electromagnetic induction agitator, which autoclave had been well dried by a

conventional method. Dehydrated n-heptanol was added to the polymerization reaction mixture in an equimolar amount relative to the amount of lithium atoms present in the polymerization reaction mixture, to thereby terminate the polymerization reaction.

The number average molecular weight of the obtained triblock copolymer was 10,100. The  $\overline{M}_w/\overline{M}_n$  ratio was 1.08. The 1,2-bond/1,4-bond molar ratio was 46/54.

#### Example 57

A well dried 5-liter high-pressure autoclave having an electromagnetic induction agitator was purged with dried nitrogen gas by a conventional method.

In an atmosphere of dried nitrogen gas, 1,333 g of cyclohexane was charged in the autoclave. The temperature of the cyclohexane was maintained at room temperature.

n-BuLi was added to the autoclave in an amount of 10.0 mmol in terms of the amount of lithium atom. To the resultant cyclohexane solution of n-BuLi was added 5.0 mmol of TMEDA (as a first complexing agent), and the resultant mixture was agitated at room temperature for 10 minutes.

The temperature of the autoclave was elevated to 40 °C and then, 7.5 mmol of TMEDA (as a second com-

plexing agent) was added to the above-obtained mixture.

100 g of 1,3-CHD was charged in the autoclave, and a polymerization reaction was conducted at 40 °C for 2 hours, to thereby form a CHD homopolymer.

5 Subsequently, 667 g of a 30 wt% solution of butadiene (Bd) in cyclohexane (Bd 200 g) was charged in the autoclave, and a polymerization reaction was further conducted at 40 °C for 2 hours, to thereby form a CHD-Bd diblock copolymer.

10 To the resultant polymerization reaction mixture containing the CHD-Bd diblock copolymer was added 100 g of 1,3-CHD, and a polymerization reaction was further conducted at 40 °C for 5 hours, to thereby form a CHD-Bd-CHD triblock copolymer.

15 The resultant polymerization reaction mixture was transferred by pressure to another 5-liter high-pressure autoclave having an electromagnetic induction agitator, which autoclave had been well dried by a conventional method. Dehydrated n-heptanol was added  
20 to the polymerization reaction mixture in an equimolar amount relative to the amount of lithium atoms present in the polymerization reaction mixture, to thereby terminate the polymerization reaction.

The number average molecular weight of the obtained triblock copolymer was 40,100. The  $\overline{M}_w/\overline{M}_n$

25

ratio was 1.15. The 1,2-bond/1,4-bond molar ratio was 51/49. The glass transition temperature ( $T_g$ ) of the CHD polymer block of the copolymer was 158 °C as measured in accordance with the DSC method.

5        The tensile strength (TS) of the obtained triblock copolymer was 14.2 MPa (1 MPa = 10.20 kg·f/cm<sup>2</sup>). The tensile elongation (TE) was 133 %. The flexural strength (FS) was 15.6 MPa and the flexural modulus (FM) was 2,957 MPa.

10        The Izod impact strength was N.B. (no break).

Example 58

A well dried 5-liter high-pressure autoclave having an electromagnetic induction agitator was purged with dried nitrogen gas by a conventional method.

15        In an atmosphere of dried nitrogen gas, 1,467 g of cyclohexane was charged in the autoclave. The temperature of the cyclohexane was maintained at room temperature.

20        n-BuLi was added to the autoclave in an amount of 10.0 mol in terms of the amount of lithium atom. To the resultant cyclohexane solution of n-BuLi was added 5.0 mmol of TMEDA (as a first complexing agent), and the resultant mixture was agitated at room temperature for 10 minutes.

25        The temperature of the autoclave was elevated to

40 °C and then, 7.5 mmol of TMEDA (as a second complexing agent) was added to the above-obtained mixture.

100 g of 1,3-CHD was charged in the autoclave, and a polymerization reaction was conducted at 40 °C for 2  
5 hours, to thereby form a CHD homopolymer.

Subsequently, 1,333 g of a 30 wt% solution of butadiene (Bd) in cyclohexane (Bd 400 g) was charged in the autoclave, and a polymerization reaction was further conducted at 40 °C for 2 hours, to thereby form a  
10 CHD-Bd diblock copolymer.

To the resultant polymerization reaction mixture containing the CHD-Bd diblock copolymer was added 100 g of 1,3-CHD, and a polymerization reaction was further conducted at 40 °C for 5 hours to thereby form a  
15 CHD-Bd-CHD triblock copolymer.

The temperature of the autoclave was elevated to 70 °C and then, the resultant polymerization reaction mixture was transferred by pressure to another 5-liter high-pressure autoclave having an electromagnetic  
20 induction agitator, which autoclave had been well dried by a conventional method. Dehydrated n-heptanol was added to the polymerization reaction mixture in an equimolar amount relative to the amount of lithium atoms present in the polymerization reaction mixture,  
25 to thereby terminate the polymerization reaction.

The number average molecular weight of the obtained triblock copolymer was 61,200. The  $\overline{M}_w/\overline{M}_n$  ratio was 1.17. The 1,2-bond/1,4-bond molar ratio was 51/49. The glass transition temperature ( $T_g$ ) of the CHD polymer block of the copolymer was 157 °C as measured in accordance with the DSC method.

The tensile strength (TS) of the obtained triblock copolymer was 19.5 MPa (1 MPa = 10.20 kg.f/cm<sup>2</sup>). The tensile elongation (TE) was 810 %.

10     Example 59

A well dried 5-liter high-pressure autoclave having an electromagnetic induction agitator was purged with dried nitrogen gas by a conventional method.

15     In an atmosphere of dried nitrogen gas, 1,500 g of cyclohexane was charged in the autoclave. The temperature of the cyclohexane was maintained at 70 °C.

1,500 g of a 10 wt% cyclohexane solution of the polymer obtained in Example 57 was added to the autoclave. To the resultant polymer solution was added a catalyst solution, which was prepared by adding titanocene dichloride (TC) and diisobutyl aluminum hydride (DIBAL-H) to cyclohexane (TC/DIBAL-H molar ratio : 1/6), as a hydrogenation catalyst, in an amount of 290 ppm, in terms of the amount of titanium atom, based on the weight of the polymer.

20

25

The autoclave was purged with hydrogen gas. The temperature of the autoclave was elevated to 160 °C and then, a hydrogenation reaction was conducted under a hydrogen pressure of 35 kg/cm<sup>2</sup>.G for 10 hours.

5        After completion of the hydrogenation reaction, removal of the solvent was conducted by a conventional method, thereby obtaining a hydrogenated CHD-Bd-CHD triblock copolymer.

10       The respective degrees of hydrogenation of the CHD polymer block and Bd polymer block were 92 mol % and 98 mol %, as determined by <sup>1</sup>H-NMR.

15       The number average molecular weight of the copolymer was 41,200. The  $\overline{M}_w/\overline{M}_n$  ratio was 1.17. The glass transition temperature (T<sub>g</sub>) of the CHD polymer block was 232 °C as measured in accordance with the DSC method.

20       The tensile strength (TS) of the obtained triblock copolymer was 19.6 MPa (1 MPa = 10.20 kg·f/cm<sup>2</sup>). The tensile elongation (TE) was 153 %. The flexural strength (FS) was 17.0 MPa and the flexural modulus (FM) was 3,254 MPa.

The Izod impact strength was N.B. (no break).

#### Example 60

25       A hydrogenation reaction was conducted in substantially the same manner as in Example 59, except that

the polymer obtained in Example 58 was used.

After completion of the hydrogenation reaction, removal of the solvent was conducted by a conventional method, to thereby obtain a hydrogenated CHD-Bd-CHD triblock copolymer.

The respective degrees of hydrogenation of the CHD polymer block and Bd polymer block were 98 mol % and 100 mol %, as determined by  $^1\text{H-NMR}$ .

The number average molecular weight was 60,900. The  $\overline{M}_w/\overline{M}_n$  ratio was 1.11. The glass transition temperature ( $T_g$ ) of the CHD polymer block was 227 °C as measured in accordance with the DSC method.

The tensile strength (TS) of the obtained triblock copolymer was 24.3 MPa (1 MPa = 10.20 kg·f/cm<sup>2</sup>). The tensile elongation (TE) was 850 %.

#### Example 61

A well dried 4-liter high-pressure autoclave having an electromagnetic induction agitator was purged with dried nitrogen gas by a conventional method.

In an atmosphere of dried nitrogen gas, 1,000 g of cyclohexane was charged in the autoclave. The temperature of the cyclohexane was maintained at 70 °C.

1,000 g of a 10 wt% cyclohexane solution of the polymer obtained in Example 57 was added to the autoclave. To the resultant polymer solution was added 10



g of a solid catalyst, which comprised 5 wt% of palladium (Pd) supported by alumina ( $\text{Al}_2\text{O}_3$ ).

5 The autoclave was purged with hydrogen gas. The temperature of the autoclave was elevated to 160 °C and then, a hydrogenation reaction was conducted under a hydrogen pressure of 55 kg/cm<sup>2</sup>.G for 6 hours.

10 After completion of the hydrogenation reaction, removal of the solvent was conducted by a conventional method, thereby obtaining a hydrogenated CHD-Bd-CHD triblock copolymer.

With respect to both of the CHD polymer block and Bd polymer block, the degree of hydrogenation was 100 mol % as determined by <sup>1</sup>H-NMR.

15 The number average molecular weight of the copolymer was 40,700. The  $\overline{M}_w/\overline{M}_n$  ratio was 1.16. The glass transition temperature (T<sub>g</sub>) of the hydrogenated CHD polymer block was 232 °C as measured in accordance with the DSC method.

20 The tensile strength (TS) of the obtained triblock copolymer was 21.4 MPa (1 MPa = 10.20 kg·f/cm<sup>2</sup>). The tensile elongation (TE) was 147 %. The flexural strength (FS) was 19.2 MPa and the flexural modulus (FM) was 3,350 MPa.

The Izod impact strength was N.B. (no break).

25 Example 62

A hydrogenation reaction was conducted in substantially the same manner as in Example 61, except that the polymer obtained in Example 58 was used.

After completion of the hydrogenation reaction, removal of the solvent was conducted by a conventional method, thereby obtaining a hydrogenated CHD-Bd-CHD triblock copolymer.

With respect to both of the CHD polymer block and Bd polymer block, the degree of hydrogenation was 100 mol % as determined by  $^1\text{H-NMR}$ .

The number average molecular weight was 62,300. The  $\overline{M}_w/\overline{M}_n$  ratio was 1.15. The glass transition temperature ( $T_g$ ) of the hydrogenated CHD polymer block was 229 °C as measured in accordance with the DSC method.

The tensile strength (TS) of the obtained triblock copolymer was 25.2 MPa (1 MPa = 10.20 kg·f/cm<sup>2</sup>). The tensile elongation (TE) was 810 %.

#### Example 63

A well dried 5-liter high-pressure autoclave having an electromagnetic induction agitator was purged with dried nitrogen gas by a conventional method.

In an atmosphere of dried nitrogen gas, 1,500 g of cyclohexane was charged in the autoclave. The temperature of the cyclohexane was maintained at 70 °C.

1,500 g of a 10 wt% cyclohexane solution of the polymer obtained in Example 56 was added to the autoclave. To the resultant polymer solution was added a catalyst solution, which was prepared by adding titanocene dichloride (TC) and n-BuLi to cyclohexane (TC/n-BuLi molar ratio : 1/1), as a hydrogenation catalyst, in an amount of 100 ppm, in terms of the amount of titanium atom, based on the weight of the polymer.

The autoclave was purged with hydrogen gas. The temperature of the autoclave was elevated to 75 °C and then, a hydrogenation reaction was conducted under a hydrogen pressure of 8 kg/cm<sup>2</sup>.G for 30 minutes.

After completion of the hydrogenation reaction, removal of the solvent was conducted by a conventional method, thereby obtaining a hydrogenated CHD-Bd-CHD triblock copolymer.

The respective degrees of hydrogenation of the CHD polymer block and Bd polymer block were 0 mol % and 100 mol %, as determined by <sup>1</sup>H-NMR.

The number average molecular weight was 10,200. The  $\overline{M}_w/\overline{M}_n$  ratio was 1.09.

#### Example 64

A well dried 5-liter high-pressure autoclave having an electromagnetic induction agitator was purged with dried nitrogen gas by a conventional method.

In an atmosphere of dried nitrogen gas, 1,947 g of cyclohexane was charged in the autoclave. The temperature of the cyclohexane was maintained at room temperature.

5       The polymerization catalyst (a complex) obtained in Example 1 was added to the autoclave in an amount of 5.0 mmol in terms of the amount of lithium atom.

      While maintaining the temperature of the autoclave at 30 °C, 3.75 mmol of TMEDA (as a second complexing agent) was added to the autoclave.

10       60 g of 1,3-CHD was charged in the autoclave, and a polymerization reaction was conducted at 30 °C for 4 hours, to thereby form a CHD homopolymer.

      To the resultant polymerization reaction mixture  
15       was added 933 g of a 30 wt% solution of butadiene (Bd) in cyclohexane (Bd 280 g), and a polymerization reaction was further conducted at 45 °C for 1 hour, to thereby form a CHD-Bd diblock copolymer.

      To the resultant polymerization reaction mixture  
20       containing the CHD-Bd diblock copolymer was added 60 g of 1,3-CHD, and a polymerization reaction was further conducted at 30 °C for 4 hours, thereby obtaining a CHD-Bd-CHD triblock copolymer.

      The resultant reaction mixture was transferred by  
25       pressure to another 5-liter high-pressure autoclave

having an electromagnetic induction agitator, which  
autoclave had been well dried by a conventional method.  
Dehydrated n-heptanol was added to the polymerization  
reaction mixture in an equimolar amount relative to the  
5 amount of lithium atoms present in the polymerization  
reaction mixture, to thereby terminate the polymeriza-  
tion reaction.

To the resultant polymer solution was added a  
catalyst solution, which was prepared by adding titano-  
10 cene dichloride (TC) and n-BuLi to cyclohexane (TC/n-  
BuLi molar ratio : 1/1), as a hydrogenation catalyst,  
in an amount of 250 ppm, in terms of the amount of  
titanium atom, based on the weight of the polymer. The  
autoclave was purged with hydrogen gas. The tempera-  
15 ture of the autoclave was elevated to 75 °C and then, a  
hydrogenation reaction was conducted under a hydrogen  
pressure of 10 kg/cm<sup>2</sup>.G for 30 minutes.

After completion of the hydrogenation reaction,  
the autoclave was cooled to room temperature, and the  
20 pressure in the autoclave was lowered to atmospheric  
pressure. The autoclave was purged with hydrogen gas,  
and n-BuLi was treated by adding methanol to the re-  
sultant reaction mixture.

To the reaction mixture was added Irganox B215  
25 (0037HX)(manufactured and sold by CIBA GEIGY, Switzer-

land) as a stabilizer, and then, removal of the solvent was conducted by a conventional method, thereby obtaining an elastic form of a hydrogenated CHD-Bd-CHD triblock copolymer.

5        The degree of hydrogenation of the CHD polymer block was 0 mol % as determined by  $^1\text{H-NMR}$ . With respect to the 1,2-vinyl bond, 1,4-cis bond and 1,4-trans bond of the Bd polymer block, the degree of hydrogenation was 100 mol % as determined by  $^1\text{H-NMR}$ . The 1,2-bond/1,4-bond molar ratio was 48/52. The glass transition temperature ( $T_g$ ) of the CHD polymer block of the  
10        copolymer was 153 °C as measured in accordance with the DSC method.

15        The number average molecular weight of the obtained triblock copolymer was 79,600. The  $\overline{M}_w/\overline{M}_n$  ratio was 1.09.

      The tensile strength (TS) of the obtained triblock copolymer was 17.8 MPa (1 MPa = 10.20 kg·f/cm<sup>2</sup>). The tensile elongation (TE) was 850 %.

20        Example 65

      A well dried 5-liter high-pressure autoclave having an electromagnetic induction agitator was purged with dried nitrogen gas by a conventional method.

25        In an atmosphere of dried nitrogen gas, 1,947 g of cyclohexane was charged in the autoclave. The tempera-

ture of the cyclohexane was maintained at room temperature.

The polymerization catalyst (a complex) obtained in Example 1 was added to the autoclave in an amount of 10.0 mmol in terms of the amount of lithium atom.

While maintaining the temperature of the autoclave at 30 °C, 7.5 mmol of TMEDA (as a second complexing agent) was added to the autoclave.

120 g of 1,3-CHD was charged in the autoclave, and a polymerization reaction was conducted at 30 °C for 4 hours, to thereby form a CHD homopolymer.

Subsequently, 933 g of a 30 wt% solution of butadiene (Bd) in cyclohexane (Bd 280 g) was charged in the autoclave, and a polymerization reaction was further conducted at 45 °C for 1 hour, to thereby obtain a CHD-Bd diblock copolymer.

To the resultant polymer solution was added silicon tetrachloride ( $\text{SiCl}_4$ ) in an amount of 2.5 mmol and then, a coupling reaction was conducted at 60 °C for 30 minutes.

To the resultant polymer solution was added Irganox B215 (0037HX)(manufactured and sold by CIBA GEIGY, Switzerland) as a stabilizer, and then, removal of the solvent was conducted by a conventional method, thereby obtaining an elastic form of a CHD-Bd-CHD triblock

copolymer. The 1,2-bond/1,4-bond molar ratio was 50/50. The glass transition temperature ( $T_g$ ) of the CHD polymer block of the copolymer was 155 °C as measured in accordance with the DSC method.

5        The number average molecular weight of the obtained triblock copolymer was 112,000. The  $\overline{M}_w/\overline{M}_n$  ratio was 2.08.

10       The tensile strength (TS) of the obtained triblock copolymer was 16.8 MPa (1 MPa = 10.20 kg·f/cm<sup>2</sup>). The tensile elongation (TE) was 600 %.

Example 66

15       A well dried 100 ml Schlenk tube was purged with dried argon gas by a conventional method. 1 g of the polymer obtained in Example 64 and 50 ml of trichlorobenzene were charged in the Schlenk tube. In an atmosphere of dried argon gas, the resultant mixture was heated to 140 °C under agitation, thereby dissolving the polymer in the trichlorobenzene.

20       To the resultant polymer solution was added tetrachloro-1,4-benzoquinone (p-chloranil) in an amount of 4 equivalents per equivalent of cyclohexene units in the polymer. A dehydrogenation reaction was conducted at 140 °C for 20 hours. After completion of the reaction, removal of the solvent was conducted by a conventional  
25       method, thereby obtaining an elastic form of a light



yellow dehydrogenated polymer.

The UV spectrum of the obtained dehydrogenated polymer was measured. It was confirmed that, in the dehydrogenated cyclic conjugated diene polymer, 89 % of the cyclohexene units in the polymer obtained in Example 64 had been converted to benzene rings.

Example 67

A well dried 5-liter high-pressure autoclave having an electromagnetic induction agitator was purged with dried nitrogen gas by a conventional method.

In an atmosphere of dried nitrogen gas, 2,400 g of cyclohexane was charged in the autoclave. The temperature of the cyclohexane was maintained at room temperature.

n-BuLi was added to the autoclave in an amount of 15.0 mmol in terms of the amount of lithium atom. To the resultant cyclohexane solution of n-BuLi was added 7.5 mmol of TMEDA (as a first complexing agent), and the resultant mixture was agitated at room temperature for 10 minutes.

The temperature of the autoclave was elevated to 40 °C and then, 11.25 mmol of TMEDA (as a second complexing agent) was added to the above-obtained mixture.

The autoclave was purged with ethylene (Et) gas. A polymerization reaction was conducted under an ethylene

pressure of 40 kg/cm<sup>2</sup>.G at 40 °C for 1 hour.

Then, the ethylene gas was evacuated and replaced by dried nitrogen gas. 300 g of 1,3-CHD was charged in the autoclave, and a polymerization reaction was further conducted at 40 °C for 7 hours, to thereby obtain an Et-CHD diblock copolymer. After that period of time, the conversion of 1,3-CHD was 98.2 mol% as measured by gas chromatography.

The temperature of the autoclave was elevated to 70 °C and then, the resultant polymerization reaction mixture was transferred by pressure to another 5-liter high-pressure autoclave having an electromagnetic induction agitator, which autoclave had been well dried by a conventional method. Dehydrated n-heptanol was added to the polymerization reaction mixture in an equimolar amount relative to the amount of lithium atoms present in the polymerization reaction mixture, to thereby terminate the polymerization reaction.

The ethylene content of the obtained diblock copolymer was 15 wt% as determined by <sup>1</sup>H-NMR.

The number average molecular weight was 23,400. The  $\overline{M}_w/\overline{M}_n$  ratio was 1.62. The 1,2-bond/1,4-bond molar ratio was 53/47. The glass transition temperature (T<sub>g</sub>) of the CHD polymer block was 157 °C as measured in accordance with the DSC method.

Example 68

A well dried 100 ml Schlenk tube was purged with dried argon gas by a conventional method. 18.0 g of cyclohexane and 2.0 g of n-hexane were charged in the Schlenk tube. While maintaining the temperature of the resultant solution at room temperature, the polymerization catalyst (a complex) obtained in Example 1 was added to the autoclave in an amount of 0.07 mmol in terms of the amount of lithium atom.

Subsequently, a 1.0 M solution of TMEDA (as a second complexing agent) in cyclohexane was added to the autoclave so as to provide a Li(in n-BuLi)/TMEDA molar ratio of 4/5, and a reaction was conducted at room temperature for 10 minutes. 1.50 g of 1,3-CHD was charged in the autoclave, and a polymerization reaction was conducted at room temperature for 3 hours in an atmosphere of dried argon gas, to thereby form a CHD homopolymer.

The resultant polymer solution was cooled to -10 °C, and 1.50 g of methyl methacrylate (MMA) was added to the polymer solution. A polymerization reaction was further conducted at -10 °C for 3 hours, thereby obtaining a CHD-MMA diblock copolymer.

To the resultant polymerization reaction mixture was added a 10 wt% solution of BHT [2,6-bis(tert-

butyl)-4-methylphenol] in methanol, to thereby terminate the polymerization reaction. Then, a large amount of a mixed solvent of methanol and hydrochloric acid was added to the polymerization reaction mixture containing the CHD-MMA diblock copolymer to thereby separate the diblock copolymer. The separated diblock copolymer was washed with methanol and then, dried at 80 °C in vacuo to thereby obtain a white mass of the CHD-MMA diblock copolymer in a yield of 81 wt%.

The number average molecular weight of the obtained CHD-MMA diblock copolymer was 34,500. The  $M_w/M_n$  ratio was 1.72. The 1,2-bond/1,4-bond molar ratio was 54/46. The glass transition temperature ( $T_g$ ) of the CHD polymer block of the copolymer was 154 °C as measured in accordance with the DSC method.

#### Example 69

A well dried 100 ml Schlenk tube was purged with dried argon gas by a conventional method. 18.0 g of cyclohexane was charged in the Schlenk tube. While maintaining the temperature of the cyclohexane at room temperature, a 1.6 M solution of n-BuLi in n-hexane was added to the cyclohexane in an amount of 0.10 mmol in terms of the amount of lithium atom. The resultant mixture was agitated for 10 minutes.

Subsequently, a 1.0 M solution of TMEDA (as a

first complexing agent) in cyclohexane was added to the above mixture so as to provide a Li(in n-BuLi)/TMEDA molar ratio of 4/2, and a reaction was conducted at room temperature for 10 minutes. The resultant reaction mixture was heated to and maintained at 40 °C to thereby obtain a complex solution.

To the above-obtained complex solution was added a 1.0 M solution of TMEDA (as a second complexing agent) in cyclohexane in an amount such that 0.075 mmol of TMEDA (as the second complexing agent) was added to the complex solution, to thereby obtain a cyclohexane solution of a complex-TMEDA mixture having a Li/TMEDA molar ratio of 4/5.

In an atmosphere of dried argon gas, 2.0 g of 1,3-CHD was added to the obtained complex-TMEDA mixture solution, and a polymerization reaction was conducted at 40 °C for 4 hours, to thereby form a CHD homopolymer.

To the resultant polymerization reaction mixture was added 2.0 g of methyl methacrylate (MMA), and a polymerization reaction was further conducted in an atmosphere of dried argon gas at 40 °C for 2.5 hours, thereby obtaining a CHD-MMA diblock copolymer.

To the resultant polymerization reaction mixture was added a 10 wt% solution of BHT [2,6-bis(tert-

butyl)-4-methylphenol] in methanol, to thereby terminate the polymerization reaction. Then, a large amount of a mixed solvent of methanol and hydrochloric acid was added to the polymerization reaction mixture containing the CHD-MMA diblock copolymer to thereby separate the diblock copolymer. The separated diblock copolymer was washed with methanol and then, dried at 60 °C in vacuo to thereby obtain a white mass of the CHD-MMA diblock copolymer in a yield of 98 wt%.

The number average molecular weight of the obtained CHD-MMA diblock copolymer was 38,700. The  $\overline{M}_w/\overline{M}_n$  ratio was 1.89. The 1,2-bond/1,4-bond molar ratio was 52/48. The glass transition temperature ( $T_g$ ) of the CHD polymer block of the copolymer was 155 °C as measured in accordance with the DSC method.

#### Example 70

A hydrogenation reaction was conducted in substantially the same manner as in Example 52, except that the polymer obtained in Example 47 was used.

After completion of the hydrogenation reaction, removal of the solvent was conducted by a conventional method, thereby obtaining a hydrogenated CHD-St-CHD triblock copolymer.

With respect to both of the CHD polymer block and St polymer block, the degree of hydrogenation was

100 mol % as determined by  $^1\text{H-NMR}$ .

The number average molecular weight was 41,000. The  $\overline{M}_w/\overline{M}_n$  ratio was 1.28. The respective glass transition temperatures ( $T_g$ ) of the hydrogenated CHD polymer block and hydrogenated styrene polymer block were 230 °C and 149 °C, as measured in accordance with the DSC method.

The flexural strength (FS) was 50.1 MPa (1 MPa = 10.20 kg·f/cm<sup>2</sup>) and the flexural modulus (FM) was 6,200 MPa.

The heat distortion temperature (HDT, 1.82 MPa) was 130 °C.

#### Example 71

A well dried 5-liter high-pressure autoclave having an electromagnetic induction agitator was purged with dried nitrogen gas by a conventional method.

In an atmosphere of dried nitrogen gas, 1,947 g of cyclohexane was charged in the autoclave. The temperature of the cyclohexane was maintained at room temperature.

60 g of 1,3-CHD and 3.0 mmol of TMEDA (as a second complexing agent) were charged in the autoclave, and the temperature of the autoclave was elevated to 40 °C.

Then, the polymerization catalyst (a complex) obtained in substantially the same manner as in Example

1 was added to the autoclave in an amount of 4.0 mmol in terms of the amount of lithium atom, and a polymerization reaction was conducted at 40 °C for 2 hours, to thereby form a CHD homopolymer.

5 Subsequently, 933 g of a 30 wt% solution of butadiene (Bd) in cyclohexane (Bd 280 g) was charged in the autoclave, and a polymerization reaction was further conducted at 40 °C for 2 hours, to thereby form a CHD-Bd diblock copolymer.

10 To the resultant polymerization reaction mixture containing the CHD-Bd diblock copolymer was added 60 g of 1,3-CHD, and a polymerization reaction was further conducted at 40 °C for 5 hours, thereby obtaining a CHD-Bd-CHD triblock copolymer.

15 The resultant polymerization reaction mixture was heated to 70 °C, and transferred by pressure to another 5-liter high-pressure autoclave having an electromagnetic induction agitator, which autoclave had been well dried by a conventional method. Dehydrated n-heptanol  
20 was added to the polymerization reaction mixture in an equimolar amount relative to the amount of lithium atoms present in the polymerization reaction mixture, to thereby terminate the polymerization reaction.

25 The number average molecular weight of the obtained triblock copolymer was 98,900. The  $\overline{M}_w/\overline{M}_n$



ratio was 1.04. The 1,2-bond/1,4-bond molar ratio was 50/50. The glass transition temperature ( $T_g$ ) of the CHD polymer block of the copolymer was 156 °C as measured in accordance with the DSC method.

- 5           The tensile strength (TS) of the obtained triblock copolymer was 19.2 MPa (1 MPa = 10.20 kg·f/cm<sup>2</sup>). The tensile elongation (TE) was 910 %.

Example 72

- 10           A well dried 5-liter high-pressure autoclave having an electromagnetic induction agitator was purged with dried nitrogen gas by a conventional method.

- 15           In an atmosphere of dried nitrogen gas, 1,947 g of cyclohexane was charged in the autoclave. The temperature of the cyclohexane was maintained at room temperature.

60 g of 1,3-CHD and 4.875 mmol of TMEDA (as a second complexing agent) were charged in the autoclave, and the temperature of the autoclave was elevated to 40 °C.

- 20           Then, the polymerization catalyst (a complex) obtained in substantially the same manner as in Example 1 was added to the autoclave in an amount of 6.5 mmol in terms of the amount of lithium atom, and a polymerization reaction was conducted at 40 °C for 2 hours, to
- 25           thereby form a CHD homopolymer.

Subsequently, 933 g of a 30 wt% solution of butadiene (Bd) in cyclohexane (Bd 280 g) was charged in the autoclave, and a polymerization reaction was further conducted at 40 °C for 2 hours, to thereby form a CHD-Bd diblock copolymer.

To the resultant polymerization reaction mixture containing the CHD-Bd diblock copolymer was added 60 g of 1,3-CHD, and a polymerization reaction was further conducted at 40 °C for 5 hours, thereby obtaining a CHD-Bd-CHD triblock copolymer.

The temperature of the autoclave was elevated to 70 °C, and the resultant polymerization reaction mixture was transferred by pressure to another 5-liter high-pressure autoclave having an electromagnetic induction agitator, which autoclave had been well dried by a conventional method. Dehydrated n-heptanol was added to the polymerization reaction mixture in an equimolar amount relative to the amount of lithium atoms present in the polymerization reaction mixture, to thereby terminate the polymerization reaction.

The number average molecular weight of the obtained triblock copolymer was 62,000. The  $\overline{M}_w/\overline{M}_n$  ratio was 1.06. The 1,2-bond/1,4-bond molar ratio was 49/51. The glass transition temperature ( $T_g$ ) of the CHD polymer block of the copolymer was 154 °C as meas-

ured in accordance with the DSC method.

The tensile strength (TS) of the obtained triblock copolymer was 17.2 MPa (1 MPa = 10.20 kg·f/cm<sup>2</sup>). The tensile elongation (TE) was 800 %.

5     Example 73

          A well dried 100 ml Schlenk tube was purged with dried argon gas by a conventional method. 27.0 g of cyclohexane was charged in the Schlenk tube. While maintaining the temperature of the cyclohexane at room  
10     temperature, the complex obtained in substantially the same manner as in Example 1, having a Li (in n-BuLi)/TMEDA molar ratio of 4/1, was added to and dissolved in the cyclohexane in an amount of 0.3 mmol in terms of the amount of lithium atom, to thereby obtain  
15     a complex solution. The complex solution was maintained at 40 °C.

          To the above-obtained complex solution was added a 1.0 M solution of TMEDA (as a second complexing agent) in cyclohexane in an amount such that 0.30 mmol of  
20     TMEDA (as the second complexing agent) was added to the complex solution, to thereby obtain a cyclohexane solution of a complex-TMEDA mixture having a Li/TMEDA molar ratio of 4/5.

          In an atmosphere of dried argon gas, 3.0 g of  
25     1,3-CHD was added to the obtained complex-TMEDA mixture

solution, and a polymerization reaction was conducted at 40 °C for 2 hours, thereby obtaining a CHD homopolymer.

To the resultant polymerization reaction mixture was added a 10 wt% solution of BHT [2,6-bis(tert-butyl)-4-methylphenol] in methanol, to thereby terminate the polymerization reaction. Then, a large amount of a mixed solvent of methanol and hydrochloric acid was added to the polymerization reaction mixture containing a desired polymer, thereby separating the desired polymer. The separated polymer was washed with methanol and then, dried at 80 °C in vacuo, thereby obtaining a white mass of the polymer in a yield of 100 wt%.

The obtained CHD homopolymer had a number average molecular weight as high as 10,200 and an  $M_w/M_n$  ratio of 1.19. The 1,2-bond/1,4-bond molar ratio was 47/53. The glass transition temperature ( $T_g$ ) of the obtained polymer was 154 °C as measured in accordance with the DSC method.

#### Example 74

A well dried 100 ml Schlenk tube was purged with dried argon gas by a conventional method. 27.0 g of cyclohexane was charged in the Schlenk tube. While maintaining the temperature of the cyclohexane at room

temperature, the complex obtained in substantially the same manner as in Example 1, having a Li (in n-BuLi)/TMEDA molar ratio of 2/2, was added to and dissolved in the cyclohexane in an amount of 0.3 mmol in terms of the amount of lithium atom, to thereby obtain a complex solution. The obtained complex solution was maintained at 40 °C.

To the above-obtained complex solution was added a 1.0 M solution of TMEDA in cyclohexane in an amount such that 0.075 mmol of TMEDA (as the second complexing agent) was added to the complex solution, to thereby obtain a cyclohexane solution of a complex-TMEDA mixture having a Li/TMEDA molar ratio of 4/5.

In an atmosphere of dried argon gas, 3.0 g of 1,3-CHD was added to the obtained complex-TMEDA mixture solution, and a polymerization reaction was conducted at 40 °C for 2 hours, thereby obtaining a CHD homopolymer.

To the resultant polymerization reaction mixture was added a 10 wt% solution of BHT [2,6-bis(tert-butyl)-4-methylphenol] in methanol, to thereby terminate the polymerization reaction. Then, a large amount of a mixed solvent of methanol and hydrochloric acid was added to the polymerization reaction mixture containing the desired polymer, thereby separating the

desired polymer. The separated polymer was washed with methanol and then, dried at 80 °C in vacuo, thereby obtaining a white mass of the polymer in a yield of 100 wt%.

5        The obtained CHD homopolymer had a number average molecular weight as high as 9,870 and an  $\overline{M_w}/\overline{M_n}$  ratio of 1.14. The 1,2-bond/1,4-bond molar ratio was 49/51. The glass transition temperature ( $T_g$ ) of the obtained polymer was 154 °C as measured in accordance  
10       with the DSC method.

Example 75

A well dried 5-liter high-pressure autoclave having an electromagnetic induction agitator was purged with dried nitrogen gas by a conventional method.

15       In an atmosphere of dried nitrogen gas, 1,500 g of cyclohexane was charged in the autoclave. The temperature of the cyclohexane was maintained at 70 °C.

1,500 g of a 10 wt% cyclohexane solution of the polymer obtained in Example 71 was added to the auto-  
20       clave. To the resultant polymer solution was added a catalyst solution, which was prepared by adding titanocene dichloride (TC) and the complex obtained in Example 1 to cyclohexane (Ti/Li molar ratio : 1/1), as a hydrogenation catalyst, in an amount of 100 ppm, in  
25       terms of the amount of titanium atom, based on the

weight of the polymer.

The autoclave was purged with hydrogen gas. The temperature of the autoclave was elevated to 75 °C and then, a hydrogenation reaction was conducted under a  
5 hydrogen pressure of 10 kg/cm<sup>2</sup>.G for 30 minutes.

After completion of the hydrogenation reaction, the autoclave was cooled to room temperature, and the pressure in the autoclave was lowered to atmospheric pressure. The autoclave was purged with nitrogen gas,  
10 and n-BuLi was treated by adding methanol to the resultant reaction mixture.

To the reaction mixture was added Irganox B215 (0037HX)(manufactured and sold by CIBA GEIGY, Switzerland) as a stabilizer and then, removal of the solvent  
15 was conducted by a conventional method, thereby obtaining an elastic form of a hydrogenated CHD-Bd-CHD tri-block copolymer.

The degree of hydrogenation of the CHD polymer block was 0 mol %. With respect to the 1,2-vinyl bond,  
20 1,4-cis bond and 1,4-trans bond of the Bd polymer block, the degree of hydrogenation was 100 mol % as determined by <sup>1</sup>H-NMR.

#### Example 76

A well dried 5-liter high-pressure autoclave  
25 having an electromagnetic induction agitator was purged

with dried nitrogen gas by a conventional method.

In an atmosphere of dried nitrogen gas, 1,500 g of cyclohexane was charged in the autoclave. The temperature of the cyclohexane was maintained at 70 °C.

5 A hydrogenation reaction was conducted in substantially the same manner as in Example 75, except that the polymer obtained in Example 72 was used.

10 The degree of hydrogenation of the CHD polymer block of the obtained hydrogenated polymer was 0 mol % as determined by  $^1\text{H-NMR}$ . With respect to the 1,2-vinyl bond, 1,4-cis bond and 1,4-trans bond of the Bd polymer block, the degree of hydrogenation was 100 mol % as determined by  $^1\text{H-NMR}$ .

Example 77

15 A well dried 100 ml Schlenk tube was purged with dried argon gas by a conventional method. 27.0 g of cyclohexane was charged in the Schlenk tube. While maintaining the temperature of the cyclohexane at room temperature, a 1.6 M solution of n-BuLi in n-hexane was  
20 added to the cyclohexane in an amount of 0.15 mmol in terms of the amount of lithium atom, to thereby obtain a solution. The temperature of the solution was maintained at 40 °C.

25 To the above-obtained solution was added a 1.0 M solution of TMEDA (as a first complexing agent) in



cyclohexane in an amount to provide a Li (in n-BuLi)/TMEDA molar ratio of 4/4, and a reaction was conducted at 40 °C for 10 minutes, to thereby obtain a complex solution.

5           To the above-obtained complex solution was added a 1.0 M solution of TMEDA (as a second complexing agent) in cyclohexane in an amount such that 0.0375 mmol of TMEDA (as the second complexing agent) was added to the complex solution, to thereby obtain a cyclohexane  
10           solution of a complex-TMEDA mixture having a Li/ TMEDA molar ratio of 4/5.

          To the obtained complex-TMEDA mixture solution was added 3.0 g of 1,3-CHD in an atmosphere of dried argon gas, and a polymerization reaction was conducted  
15           at 40 °C for 4 hours. To the resultant polymerization reaction mixture was added a 10 wt% solution of BHT [2,6-bis(tert-butyl)-4-methylphenol] in methanol, to thereby terminate the polymerization reaction. Then, a large amount of a mixed solvent of methanol and hydro-  
20           chloric acid was added to the polymerization reaction mixture containing a CHD homopolymer, to thereby separate the CHD homopolymer. The separated polymer was washed with methanol and then, dried at 80 °C in vacuo to thereby obtain a mass of the CHD homopolymer in a  
25           yield of 100 wt%.

The 1,2-bond/1,4-bond molar ratio was 52/48.

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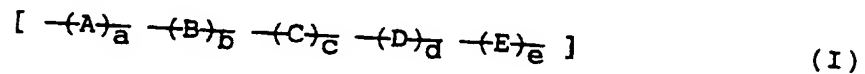
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Industrial Applicability

The cyclic conjugated diene polymer of the present invention has not only a relatively high 1,2-bond/1,4-bond molar ratio, but also a relatively narrow molecular weight distribution, so that it exhibits excellent thermal properties, mechanical properties and excellent functions. The cyclic conjugated diene polymer of the present invention can be advantageously used either singly or in combination with inorganic materials as well as another resin material, depending on the intended use. Further, if desired, by subjecting the cyclic conjugated diene polymer of the present invention to at least one reaction selected from the group consisting of hydrogenation, halogenation, hydrohalogenation, alkylation, arylation, a ring-opening reaction and dehydrogenation, various functions can be imparted to the polymer. The cyclic conjugated diene polymer of the present invention can be produced by the novel method of the present invention in which a living anion polymerization of a cyclic conjugated diene monomer or of a cyclic conjugated diene monomer and a comonomer copolymerizable therewith is performed in the presence of a unique catalyst.

Claims

1. A cyclic conjugated diene polymer comprising a main chain represented by the following formula (I):



wherein A to E are monomer units constituting said main chain in which monomer units A to E are arranged in any order, and a to e are, respectively, weight percentages of monomer units A to E, based on the total weight of monomer units A to E; wherein

A is selected from the class consisting of cyclic conjugated diene monomer units,

B is selected from the class consisting of chain conjugated diene monomer units,

C is selected from the class consisting of vinyl aromatic monomer units,

D is selected from the class consisting of polar monomer units, and

E is selected from the class consisting of an ethylene monomer unit and  $\alpha$ -olefin monomer units;

wherein:

a to e satisfy the following requirements:

$$a + b + c + d + e = 100,$$

$$0.1 \leq a \leq 100,$$

$$0 \leq b < 100,$$

$$0 \leq c < 100,$$

5  $0 \leq d < 100,$  and

$$0 \leq e < 100; \text{ and}$$

wherein said A monomer units are bonded in  
said main chain by a 1,2-bond and a 1,4-bond,  
wherein the molar ratio of the 1,2-bond to  
10 the 1,4-bond is from 40/60 to 90/10,  
said cyclic conjugated diene polymer having a  
number average molecular weight of 500 to 5,000,000.

2. The cyclic conjugated diene polymer according to  
15 claim 1, which is a block copolymer.

3. The cyclic conjugated diene polymer according to  
claim 1 or 2, which has a glass transition temperature  
(T<sub>g</sub>) of 150 °C or more.

20

4. The cyclic conjugated diene polymer according to  
claim 2, wherein said block copolymer contains a poly-  
mer block having a glass transition temperature (T<sub>g</sub>) of  
150 °C or more.

25

5. The cyclic conjugated diene polymer according to any one of claims 2 to 4, which is an at least-tri-block copolymer.
- 5 6. The cyclic conjugated diene polymer according to any one of claims 2 to 5, which is a block copolymer having a polymer block containing at least two A monomer units.
- 10 7. The cyclic conjugated diene polymer according to any one of claims 2 to 5, which is a block copolymer having a polymer block consisting of at least two A monomer units.
- 15 8. The cyclic conjugated diene polymer according to any one of claims 2 to 4, which is an at least-di-block copolymer comprising at least one polymer block consisting of at least two A monomer units, and at least one polymer block consisting of monomer units of at least one type selected from the group of said B to said E.
- 20
- 25 9. The cyclic conjugated diene polymer according to any one of claims 2 to 4, which is a diblock copolymer comprising one X polymer block containing at least one

A monomer unit, and one Y polymer block comprised mainly of monomer units of at least one type selected from said B and said E, wherein the weight ratio of said X block to said Y block is from 1/99 to 99/1.

5

10. The cyclic conjugated diene polymer according to claim 5, which is an at least-tri-block copolymer comprising at least two X blocks each containing at least one A monomer unit, and at least one Y block comprised mainly of monomer units of at least one type selected from said B and said E, wherein the weight ratio of said X blocks to said Y block is from 1/99 to 99/1.

11. The cyclic conjugated diene polymer according to claim 5, which is a triblock copolymer comprising two X blocks containing at least one A monomer unit, and one Y block comprised mainly of monomer units of at least one type selected from said B and said E.

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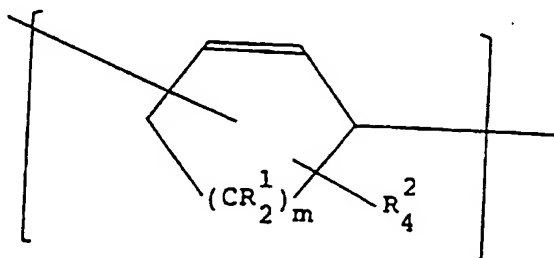
12. The cyclic conjugated diene polymer according to claim 10, wherein said at least-tri-block copolymer has a configuration represented by a formula selected from the group consisting of  $X - (Y - X)_p$ ,  $(X - Y)_q$ ,  $Y - (X - Y)_q$ ,  $[(Y - X)_{\overline{p}}]_{\overline{q}}$ ,  $[(X - Y)_{\overline{p}}]_{\overline{q}}$ ,  $[(Y -$

25

$X)_p-Y-\overline{\overline{q}}$ , and  $[(X-Y)_p-X-\overline{\overline{q}}]$  in which X and Y are as defined above, p is an integer of 1 or more, and q is an integer of 2 or more.

- 5 13. The cyclic conjugated diene polymer according to any one of claims 1 to 12, wherein said A monomer unit is selected from the class consisting of monomer units represented by the following formula (II):

10



(II).

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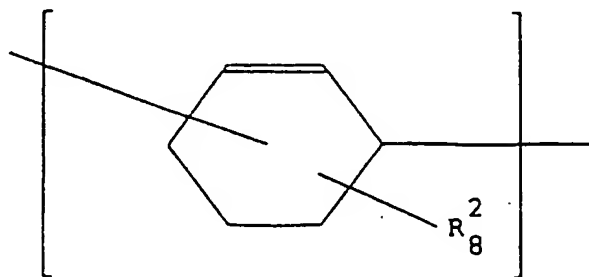
20 wherein m is an integer of from 1 to 4, each  $R^1$  independently represents a hydrogen atom, a halogen atom, a  $C_1-C_{20}$  alkyl group, a  $C_2-C_{20}$  unsaturated aliphatic hydrocarbon group, a  $C_5-C_{20}$  aryl group, a  $C_3-C_{20}$  cycloalkyl group, a  $C_4-C_{20}$  cyclodienyl group or a 5 to 10-membered heterocyclic group having at

25 least one nitrogen, oxygen or sulfur atom as



a heteroatom, and each  $R^2$  independently represents a hydrogen atom, a halogen atom, a  $C_1-C_{20}$  alkyl group, a  $C_2-C_{20}$  unsaturated aliphatic hydrocarbon group, a  $C_5-C_{20}$  aryl group, a  $C_3-C_{20}$  cycloalkyl group, a  $C_4-C_{20}$  cyclodienyl group or a 5 to 10-membered heterocyclic group having at least one nitrogen, oxygen or sulfur atom as a heteroatom, or each  $R^2$  independently represents a bond or a group such that two  $R^2$  groups together form a bridge represented by the formula  $-(CR_2^3)_n$  in which  $R^3$  has the same meaning as defined for  $R^1$  and  $n$  is an integer of from 1 to 10.

14. The cyclic conjugated diene polymer according to claim 13, wherein said A monomer unit is selected from the class consisting of monomer units represented by the following formula (III):



(III)

wherein each  $R^2$  is as defined for formula (II).

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15. The cyclic conjugated diene polymer according to claim 13, wherein said A monomer unit is at least one member selected from the class consisting of a 1,3-cyclopentadiene monomer unit, a 1,3-cyclohexadiene monomer unit, a 1,3-cyclooctadiene monomer unit, and derivatives thereof.

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16. A cyclic conjugated diene polymer according to claim 14, wherein said A monomer unit is a 1,3-cyclohexadiene monomer unit or a derivative thereof.

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17. The cyclic conjugated diene polymer according to claim 14, wherein said A monomer unit is a 1,3-cyclohexadiene monomer unit.

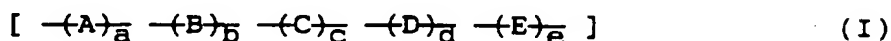
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18. A polymer produced by subjecting a cyclic conjugated diene polymer of any one of claims 1 to 17 to at least one reaction selected from the group consisting of hydrogenation, halogenation, hydrohalogenation, alkylation, arylation, ring-opening reactions and dehy-

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drogenation.

19. A method for producing a cyclic conjugated diene polymer comprising a main chain represented by the following formula (I):



wherein A to E are monomer units constituting said main chain in which monomer units A to E are arranged in any order, and a to e are, respectively, weight percentages of monomer units A to E, based on the total weight of monomer units A to E; wherein

A is selected from the class consisting of cyclic conjugated diene monomer units,

B is selected from the class consisting of chain conjugated diene monomer units,

C is selected from the class consisting of vinyl aromatic monomer units,

D is selected from the class consisting of polar monomer units, and

E is selected from the class consisting of an ethylene monomer unit and  $\alpha$ -olefin monomer units; and

wherein:

a to e satisfy the following requirements:

$$a + b + c + d + e = 100,$$

$$0.1 \leq a \leq 100,$$

$$0 \leq b < 100,$$

5  $0 \leq c < 100,$

$$0 \leq d < 100, \text{ and}$$

$$0 \leq e < 100;$$

10 said cyclic conjugated diene polymer having a number average molecular weight of 500 to 5,000,000, which comprises:

providing a complex of at least one organometallic compound containing a metal belonging to Group IA of the Periodic Table with at least one first complexing agent, and

15 polymerizing at least one cyclic conjugated diene monomer, or at least one cyclic conjugated diene monomer and at least one comonomer copolymerizable therewith, in the presence of a catalyst comprising a mixture of said complex and at least one second complexing agent,

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said comonomer being selected from the class consisting of chain conjugated diene monomers, vinyl aromatic monomers, polar monomers, an ethylene monomer, and  $\alpha$ -olefin monomers.

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20. The method according to claim 19, wherein each of said first complexing agent and said second complexing agent is independently an organic compound containing at least one element selected from the group consisting of oxygen (O), nitrogen (N), sulfur (S) and phosphorus (P).

21. The method according to claim 19, wherein each of said first complexing agent and said second complexing agent is independently an organic compound selected from the group consisting of an ether, a metal alkoxide, an amine and a thioether.

22. The method according to claim 19, wherein each of said first complexing agent and said second complexing agent is independently an ether or an amine.

23. The method according to claim 19, wherein each of said first complexing agent and said second complexing agent is independently an amine.

24. The method according to claim 19, wherein each of said first complexing agent and said second complexing agent is independently a diamine.

25. The method according to claim 19, wherein each of said first complexing agent and said second complexing agent is independently an aliphatic diamine.
- 5 26. The method according to claim 19, wherein each of said first complexing agent and said second complexing agent is independently a tertiary amine.
- 10 27. The method according to claim 24, wherein said diamine is selected from the group consisting of tetramethylethylenediamine (TMEDA) and diazabicyclo[2,2,2]-octane (DABCO).
- 15 28. The method according to any of claims 19 to 27, wherein said organometallic compound containing a metal belonging to Group IA of the Periodic Table is an organolithium compound.
- 20 29. The method according to claim 19, wherein said organometallic compound containing a metal belonging to Group IA of the Periodic Table is an organolithium compound selected from the group consisting of normal butyllithium (n-BuLi), secondary butyllithium (s-BuLi) and tertiary butyllithium (t-BuLi), and each of said
- 25 first complexing agent and said second complexing agent

is independently selected from the group consisting of tetramethylethylenediamine (TMEDA) and diazabicyclo[2,2,2]-octane (DABCO).

5 30. The method according to any of claims 19 to 29, wherein said complex is one which is prepared by reacting said organometallic compound containing a metal belonging to Group IA of the Periodic Table with said first complexing agent in a molar ratio represented by  
10 the following formula:

$$A_1/B_1 = 200/1 \text{ to } 1/100$$

wherein  $A_1$  represents the molar amount of the Group IA metal contained in said organometallic compound used for the reaction, and  $B_1$   
15 represents the molar amount of said first complexing agent used for the reaction.

31. The method according to any one of claims 19 to 29, wherein said complex is comprised of said organometallic compound containing a metal belonging to Group  
20 IA metal of the Periodic Table and said first complexing agent in a molar ratio represented by the following formula:

$$A_2/B_2 = 1/0.25 \text{ to } 1/1$$

25 wherein  $A_2$  represents the molar amount of the

Group IA metal contained in said organometallic compound constituent of said complex, and B2 represents the amount of said first complexing agent constituent of said complex.

5

32. The method according to any one of claims 19 to 29, wherein, in said catalyst, said organometallic compound, said first complexing agent and said second complexing agent are present in a molar ratio relationship represented by the following formula:

10

$$A_3/B_3 = 100/1 \text{ to } 1/200$$

wherein  $A_3$  represents the molar amount of the Group IA metal contained in said organometallic compound, and  $B_3$  represents the total molar amount of said first complexing agent and said second complexing agent.

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## INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP95/02362

## A. CLASSIFICATION OF SUBJECT MATTER

Int. Cl<sup>6</sup> C08F4/46, 210/00, 212/00, 220/00, 32/00, 236/04, 293/00  
According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

Int. Cl<sup>6</sup> C08F4/00-4/82, 210/00-210/18, 212/00-212/36, 220/00-220/70, 32/00-32/08, 236/00-236/22, 293/00

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

CAS ONLINE, WPI/L

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP, 58-216243, A (Japan Synthetic Rubber Co., Ltd.), December 15, 1983 (15. 12. 83), Claim, lines 6 to 17, upper left column, lines 10 to 15, upper right column, page 3 (Family: none)	1 - 32
P	WO, 94/28038, A1 (Asahi Chemical Industry Co., Ltd.), December 8, 1994 (08. 12. 94), Claim (Family: none)	1 - 32
A	JP, 63-230707, A (Nippon Zeon Co., Ltd.), September 27, 1988 (27. 09. 88), Claim (Family: none)	18
A	JP, 58-71903, A (Imperial Chemical Industries PLC.), April 28, 1983 (28. 04. 83), Claim & EP, 76605, A1 & US, 4476296, A	1 - 18

☐ Further documents are listed in the continuation of Box C.

☐ See patent family annex.

\* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date of the document which may throw doubt on priority claim(s) or which is cited to establish the publication date of another claim or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"T" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, each combination being obvious to a person skilled in the art

"A" document member of the same patent family

Date of the actual completion of the international search  
January 8, 1996 (08. 01. 96)

Date of mailing of the international search report  
January 30, 1996 (30. 01. 96)

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